

# Wetting Behavior of Pentane on Water. The Analysis of Temperature Dependence

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Received: April 28, 2007; In Final Form: June 15, 2007

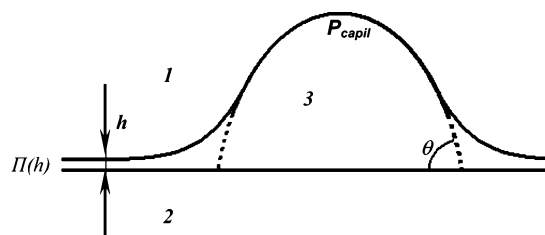
The temperature dependence of wetting behavior for pentane on water is analyzed from the standpoint of the Derjaguin–Frumkin theory. The joint action of two mechanisms of surface forces, the van der Waals and the image charge interactions, are considered to calculate the isotherms of the disjoining pressure. To analyze the temperature influence on the magnitude of van der Waals forces, we have used the exact Dzyaloshinsky, Lifshitz, and Pitaevsky equation. It is shown that image forces, arising due to the restricted solubility of water in pentane, decay much faster with increasing the film thickness and can be considered as short ranged in comparison to the van der Waals forces. The competitive action of the image charge and the van der Waals forces provides the plausible explanation of the temperature dependence of wetting in the system under consideration.

## 1. Introduction

Wetting films of alkanes on a water surface represent one of the most simple and convenient, nevertheless not of less interest, model systems for study of the surface forces in thin liquid interlayers. The Derjaguin–Frumkin theory of wetting<sup>1,2</sup> allows one to relate the wetting behavior of liquid 3 on top of the substrate 2 (it might be another liquid or a solid) with the thickness dependence of the surface forces acting between the vapor phase 1 and substrate 2, confining the film of liquid 3 (Figure 1). Provided such dependence (conventionally referred to as an isotherm of disjoining pressure) is available, one can assess the stability of wetting films and calculate the macroscopic contact angle between the liquid and the substrate. An inverse problem can be solved as well, namely, on the basis of the measurement of the contact angle and the wetting films thickness one can make conclusions about a character of surface forces acting in the system under consideration. Both above-mentioned problems will be discussed in the section 2 of this paper.

Coming back to the main object of this study, it is necessary to note that the numerous experimental data indicate the complex wetting behavior of hydrocarbons on water. Sometimes the experimental observations of different authors contradict each other.<sup>3–7</sup> The nonspreading behavior of alkanes starting from heptane is well explained qualitatively<sup>8,9</sup> on the basis of the Dzyaloshinsky, Lifshitz, and Pitaevsky (DLP) theory.<sup>10</sup> As for the lower alkanes, the results of theoretical description of their wetting behavior<sup>4,8,9</sup> on the basis of macroscopic theory of dispersion forces were drastically dependent on the approach used to construct the frequency dependence of the dielectric permittivity. The disagreement between the estimations of different authors for the van der Waals contribution to the stability of wetting films not only was quantitative but also allowed contrary conclusions about the film stability to be drawn.

Another important point, namely, an analysis of the temperature dependence of van der Waals contribution into the alkane wetting film stability and wetting behavior was also addressed in the literature both experimentally and theoretically.<sup>5,11,12</sup> In



**Figure 1.** For a wetting film being in the equilibrium with a sessile drop the disjoining pressure in the film should be equal to the capillary pressure in the drop.

the above papers the theoretical analysis was based on the method of rough estimation of the Hamaker constants, proposed by Israelachvili.<sup>13</sup> This estimation is based on the assumption that the behavior of dielectric permittivities,  $\epsilon(i\xi)$ , of contacting media as the function of imaginary frequency,  $i\xi$ , is determined by only one band of electronic absorption

$$\epsilon(i\xi) \approx 1 + \frac{(n^2 - 1)}{1 + \xi^2/\omega_e^2} \quad (1)$$

where  $n$  is the refractive index of the medium in the visible region and  $\omega_e$  is the main electronic absorption frequency in the ultraviolet region.

With the same value of absorption frequencies,  $\omega_e$ , for two contacting media (i.e., for both water and alkane), the approximate equation for the Hamaker constant  $A_{132}$  of nonretarded van der Waals forces of interaction for two macroscopic phases 1 and 2 across a medium 3 takes the form

$$A_{132} \approx \frac{3k_B T}{4} \left( \frac{\epsilon_{10} - \epsilon_{30}}{\epsilon_{10} + \epsilon_{30}} \right) \left( \frac{\epsilon_{20} - \epsilon_{30}}{\epsilon_{20} + \epsilon_{30}} \right) + \frac{3\hbar\omega_e}{8\sqrt{2}} \frac{(n_1^2 - n_3^2)(n_2^2 - n_3^2)}{(n_1^2 + n_3^2)^{1/2}(n_2^2 + n_3^2)^{1/2}[(n_1^2 + n_3^2)^{1/2} + (n_2^2 + n_3^2)^{1/2}]} \quad (2)$$

Here  $k_B$  and  $\hbar$  are the Boltzmann and Planck constants, respectively,  $T$  is the temperature, and  $\epsilon_{j0}$  is the static value of dielectric permittivity for  $j$ th medium. So the only parameters of contacting phases used for calculation of temperature

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dependence are the value of frequency of electronic absorption, refractive indices, and static values of dielectric permittivities of contacting media.

The validity of the application of above approach to the analysis of temperature dependence of wetting behavior of alkanes on water causes essential doubts for reasons already discussed in ref 13. First, the values of absorption frequencies  $\omega_e$  for contacting media may essentially differ from each other, where the magnitude of the nonretarded Hamaker constant is very sensitive to the above parameters.<sup>8,9,14</sup> Second, for polar media (and especially for water), the absorption bands in the microwave and infrared regions significantly contribute to both the frequency behavior of dielectric permittivity and the magnitude of dispersion forces. Finally, eq 2 was obtained by the approximation of small thicknesses in the nonretarded limit, so it could hardly be used to describe the wetting transition, accompanied by film thickening from monolayer thicknesses to hundreds of angstroms. Therefore in section 3 we will present the analysis of the temperature influence on the magnitude of the van der Waals (molecular) forces based on the exact DLP equations and take into account the detailed presentation of dielectric permittivity spectra of the contacting phases. It will be shown, that van der Waals forces alone cannot account for the observed wetting behavior of pentane on water. Thus in section 4 we will invoke another mechanism of surface forces, related to the solubility of water (which is used as a substrate) in alkanes. It will be shown that an appreciable force might arise due to the adsorption of solute molecules and interaction of dipoles of water molecules in the adsorbed layer with their images in confining phases. The competitive action of van der Waals and image charge forces provides the plausible explanation of temperature dependence of wetting in the system.

## 2. The Derjaguin–Frumkin Theory of Wetting and Surface Forces

Derjaguin and Frumkin (for a detailed description see ref 1) have considered the peculiarities of the three-phase equilibrium in a system containing a solid (liquid) substrate, a bulk liquid meniscus (either a meniscus near the wall or a sessile drop), and a vapor phase. It was shown that depending on the character of surface forces acting in the system, three types of equilibrium might be established: between the meniscus and the dry substrate, between the meniscus and the substrate covered by wetting or adsorption film, and the substrate covered by a thick film of bulk liquid. Two former cases correspond to the partial wetting, while the latter one is characteristic for the complete wetting.

Derjaguin<sup>1</sup> has derived the relation between the equilibrium value of the macroscopic contact angle  $\theta_0$  and the isotherm of disjoining pressure  $\Pi(h)$ , characterizing the combined action of different mechanisms<sup>15</sup> of surface forces

$$\sigma_{LV} \cos \theta_0 = \sigma_{LV} + \Pi(h_0) h_0 + \int_{h_0}^{\infty} \Pi(h) dh \quad (3)$$

where  $h_0$  is the thickness of a wetting film being in equilibrium with the meniscus of a bulk liquid or with a sessile drop,  $\sigma_{LV}$  is the surface tension of liquid, and  $\Pi(h_0)$  is the disjoining pressure in the wetting film, equal to the capillary pressure in the meniscus or the drop (Figure 1).

Having in mind the thermodynamic condition of thin film stability<sup>16</sup>

$$\frac{\partial \Pi(h)}{\partial h} < 0 \quad (4)$$

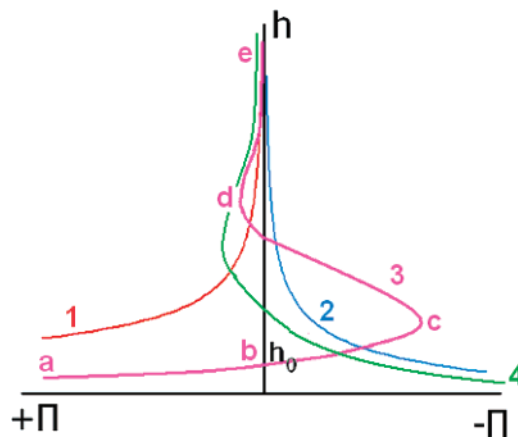


Figure 2. Different types of the isotherms of the disjoining pressure.

one can relate the peculiarities of wetting behavior in the three-phase system with the type of the isotherm of disjoining pressure. Here we will demonstrate briefly this interrelation with an example of four types of isotherms, shown in Figure 2. The isotherm of type 1 is characterized by a positive disjoining pressure and meets condition 4 in the whole range of thicknesses. So having the isotherm of such a type in the system under consideration, we can expect equilibrium between a wetting film and unsaturated vapor or between a wetting film and bulk liquid meniscus with positive capillary pressure. Due to negative sign of the capillary pressure in a sessile drop (capillary pressure is determined here as  $P_{\text{capil}} = P_{\text{air}} - P_{\text{liquid}}$ ), no equilibrium can exist between the drop of liquid and the wetting film; hence the sessile drop will spread over the substrate, forming a macroscopically thick film with the disjoining pressure tending to zero.

The contact angle, calculated according to the eq 3, turns to zero, and the system is characterized by complete wetting. In contrast, the isotherm of type 2 corresponds to the negative disjoining pressure in the whole range of thicknesses and does not satisfy condition 4. So if the three-phase system is characterized by isotherm of type 2, the sessile drop of liquid cannot be in equilibrium with a wetting film and will coexist with a dry substrate. Due to a negative value of the integral in eq 3, the contact angle will differ from zero and its magnitude is determined by the area under the isotherm of disjoining pressure. Thus a three-phase system with an isotherm of type 2 will demonstrate either partial wetting or nonwetting.

For another case of partial wetting, when the liquid drop coexists with a wetting film (in the literature this case is sometimes referred to as a pseudopartial wetting), the system should be characterized by a so-called S-type isotherm, for example, of type 3 in Figure 2. This follows from the fact that the capillary pressure in the drop is negative and the drop can coexist in the equilibrium with the film only in the case of a negative value of disjoining pressure inside the latter. Thus the presence of a negative branch of the isotherm of disjoining pressure jointly with the fulfillment of eq 3 can be considered as a necessary condition for creation of a finite contact angle between the wetting film and the drop. For the isotherm of type 3 the above conditions are held simultaneously for the range of thicknesses from point b to point c (see Figure 2). The ranges of thicknesses [a,b] and [d,e] correspond to the equilibrium between a wetting film and unsaturated vapor or between a wetting film and bulk liquid meniscus with positive capillary pressure. The thicknesses in the ranges [a,b] and [d,e] are associated to  $\alpha$  and  $\beta$  wetting films, respectively. Typically only one state of films (either  $\alpha$  or  $\beta$ ) is stable, whereas another one

is metastable. But as we have shown earlier,<sup>17</sup> if the difference between the free energies of two states at a definite disjoining pressure is less than  $k_B T$ , then the unsaturated vapor might coexist with islands of  $\alpha$ - and  $\beta$ -wetting films simultaneously. Finally the wetting films with thicknesses in the range [c,d] are unstable.

To apply the Derjaguin and Frumkin approach for the analysis of wetting behavior of alkanes on water, it is necessary to know the isotherm of disjoining pressure for the system under investigation as well as its temperature dependence. All the following analyses will be demonstrated with an example of pentane films on water, as the most studied system. Before proceeding to the exact calculations of the isotherm of disjoining pressure, it is necessary to stress the following. As follows from the data of Ragil et al.,<sup>5</sup> two types of equilibria were observed for pentane on water in the temperature range between 20 and 60 °C. Namely, pentane wetting film might be in equilibrium both with the undersaturated pentane vapor at positive disjoining pressure and with a lens of pentane on the top of the water substrate at negative pressure. The existence of the two above types of equilibria unambiguously indicates that the system under consideration is characterized by an isotherm of disjoining pressure of type 3.

### 3. The Calculations of van der Waals Forces at Different Temperatures

In general the molecular (van der Waals) component of disjoining pressure,  $\Pi_m(h)$ , equal to the specific force of interaction between two macroscopic bodies through uniform plane-parallel liquid interlayer having thickness  $h$ , might be computed as<sup>10</sup>

$$\Pi_m(h) = -\frac{k_B T}{\pi c^3} \sum_{N=0}^{\infty} \xi_N^3 \epsilon_3^{(3/2)} \int_1^{\infty} p^2 \left\{ \frac{(s_1 + p)(s_2 + p)}{(s_1 - p)(s_2 - p)} \exp \left( \frac{2p \xi_N h \epsilon_3^{(1/2)}}{c} \right) - 1 \right\}^{-1} + \left[ \frac{(s_1 + ap)(s_2 + bp)}{(s_1 - ap)(s_2 - bp)} \exp \left( \frac{2p \xi_N h \epsilon_3^{(1/2)}}{c} \right) - 1 \right]^{-1} \right\} dp \quad (5)$$

where  $c$  is the velocity of light,  $p$  is integration variable,  $\xi_N = 2\pi k_B T N / \hbar$ , with natural number  $N$ ,  $s_1 = (a - 1 + p^2)^{1/2}$ ,  $s_2 = (b - 1 + p^2)^{1/2}$ ,  $a = \epsilon_1/\epsilon_3$ ,  $b = \epsilon_2/\epsilon_3$ ,  $\epsilon_1(i\xi_N)$ ,  $\epsilon_2(i\xi_N)$ , and  $\epsilon_3(i\xi_N)$  are the imaginary frequency dependencies of dielectric permittivities of phases 1 and 2 and separating interlayer 3, respectively. The prime at the summation sign indicates that the first term (with  $N = 0$ ) has to be taken half-weighted. Note that the straightforward substitution of  $N = 0$  into eq 2 leads to uncertainty since  $\xi_N$  turns out to be zero, while the integral over  $dp$  diverges. However the appropriate replacement of variables<sup>10</sup> reveals the finite value of the term under consideration. The contribution from this zero frequency term might be quite important in the limiting case of thin film thickness, and it was calculated according to the conventional procedure<sup>8</sup>

$$\Pi_{\xi=0}(h) \approx \frac{k_B T}{8\pi h^3} \sum_s \frac{\left[ \left( \frac{\epsilon_{10} - \epsilon_{30}}{\epsilon_{10} + \epsilon_{30}} \right) \left( \frac{\epsilon_{20} - \epsilon_{30}}{\epsilon_{20} + \epsilon_{30}} \right) \right]^s}{s^3} \quad (6)$$

To make the quantitative prediction of the disjoining pressure, we have used the Ninham–Parsegian<sup>18</sup> representation of the dielectric permittivities  $\epsilon_j(i\xi_N)$

$$\epsilon(i\xi) = 1 + \frac{C_{\text{MICRO}}}{1 + (\xi/\omega_{\text{MICRO}})^2} + \frac{C_{\text{IR}}}{1 + (\xi/\omega_{\text{IR}})^2} + \frac{C_{\text{UV}}}{1 + (\xi/\omega_{\text{UV}})^2} \quad (7a)$$

$$\epsilon(i\xi) = 1 + \frac{C_{\text{IR}}}{1 + (\xi/\omega_{\text{IR}})^2} + \frac{C_{\text{UV}}}{1 + (\xi/\omega_{\text{UV}})^2} \quad (7b)$$

Here  $\omega_{\text{MICRO}}$ ,  $\omega_{\text{IR}}$ , and  $\omega_{\text{UV}}$  are the characteristic relaxation frequencies in microwave, infrared, and ultraviolet regions, respectively, and  $C_{\text{MICRO}}$ ,  $C_{\text{IR}}$ , and  $C_{\text{UV}}$  are the constants associated with strengths of corresponding oscillators.

Equation 7a was used to represent the  $\epsilon(i\xi_N)$  for water, whereas for pentane eq 7b was chosen.<sup>8</sup> The procedure for calculating the constants  $C_{\text{IR}}$ ,  $C_{\text{UV}}$ , and  $C_{\text{MICRO}}$  was described in detail by Hough and White.<sup>8</sup> Thus, according to their method we have determined  $C_{\text{UV}}$  and  $\omega_{\text{UV}}$  from the “Cauchy” plot representation of frequency dependence of refractive index data,  $n(\omega)$ ;  $C_{\text{IR}}$  and  $C_{\text{MICRO}}$  were calculated according to the relations

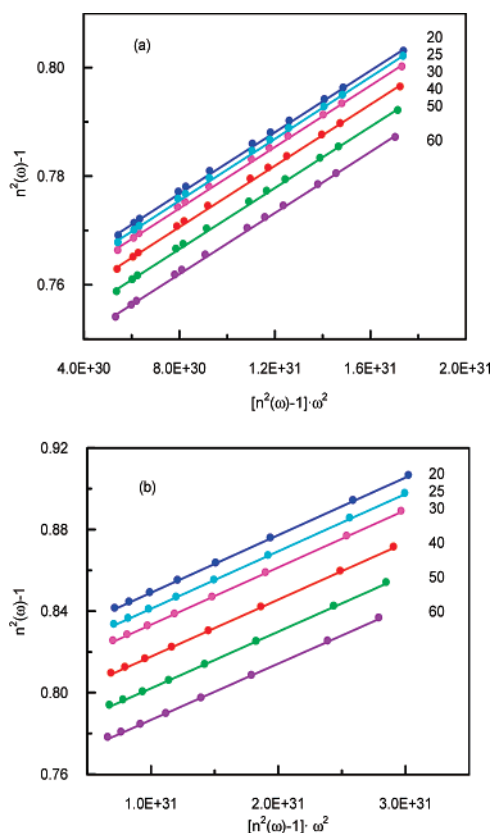
$$C_j = \epsilon_j(\text{before}) - \epsilon_j(\text{after}) \quad (8)$$

where  $\epsilon_j(\text{before})$  and  $\epsilon_j(\text{after})$  denote the values of dielectric response in the transparent regions before and after the relaxation frequency  $\omega_j$  ( $j = \text{IR, MICRO}$ ).

The representation (7b) for pentane does not cause any complication, because pentane exhibits very weak absorption in the microwave region and the only significant absorption band in the infrared, corresponding to C–H stretching vibration. The analysis of water spectra at various temperatures indicates that the values of  $C_{\text{MICRO}}$  and  $\omega_{\text{MICRO}}$  can be evaluated quite reliably, whereas the infrared region is represented by at least four strongly absorbing and overlapping bands. The description of such a spectrum by eq 7a means the replacement of all these bands by a single effective band. While the estimation of  $C_{\text{IR}}$  for such an effective band in accordance with eq 8 is straightforward, the determination of the corresponding value for  $\omega_{\text{IR}}$  meets some difficulties. In our calculations, we have used the following procedure. At the first step, we used the five-band infrared region representation of Gingell and Parsegian<sup>19</sup> jointly with  $C_{\text{UV}}$  and  $\omega_{\text{UV}}$  determined from the “Cauchy” plot representation of refractive index data to compute the molecular forces in the system at  $T = 20$  °C. At the second step, we have adjusted the value of  $\omega_{\text{IR}}$  in the representation (7a) to achieve the same magnitude of molecular forces as one obtained at the first step. This procedure provided us such parameters of the effective IR absorption band which reproduce the behavior of dielectric permittivity of water in the infrared region equivalent to the more detailed five-band representation.<sup>18</sup> The analysis of behavior of real IR spectra of water at different temperatures allows the conclusion that the variation of temperature causes the change in the magnitude of  $C_{\text{IR}}$ , while the effective band position  $\omega_{\text{IR}}$  is almost invariant.

In Figure 3 are displayed the Cauchy plots for water and pentane at different temperatures using  $n(\omega)$  data taken from the literature.<sup>20,21</sup> The values of parameters of eqs 7a and 7b used for the calculation of van der Waals forces are summarized in Table 1.

With the parameters presented in Table 1, the isotherms of molecular component of the disjoining pressure were calculated on the basis of eq 5 for different temperatures. For 20, 25, 30,



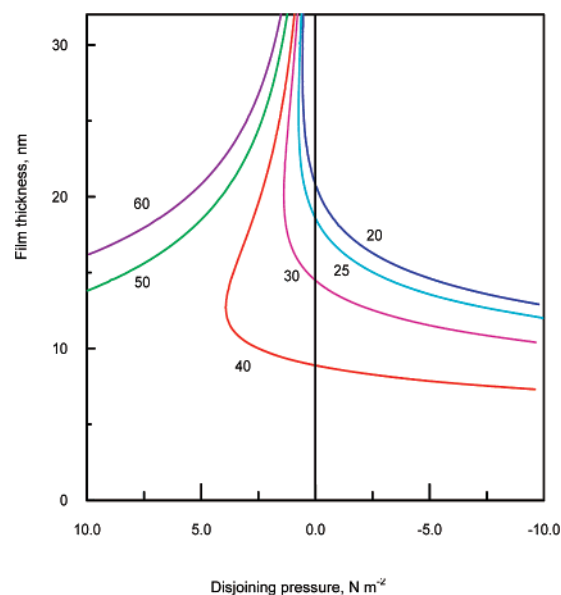
**Figure 3.** “Cauchy” plot representation of frequency dependences of refractive index data for water (a) and pentane (b) at different temperatures: points, experimental data; solid lines, the least-squares linear fits. The numbers at the lines indicate the temperatures in °C.

and 40 °C the thickness dependences of molecular forces are described by the isotherms of type 4 (Figure 2), whereas for 50 and 60 °C type 1 is characteristic. The Hamaker constants,  $A_{132}$ , for pentane film confined by air and water, which quantitatively characterize the van der Waals forces in the limit of small thicknesses, are listed in Table 2, and the thick film behavior is presented in Figure 4.

Thus, the analysis of calculation results indicates that at any of the temperatures considered the van der Waals interactions do not provide the isotherm of type 3, necessary to describe the experimental findings.<sup>5</sup>

#### 4. Image-Charge Contribution to the Wetting Behavior of Pentane Wetting Films on Water

As shown above, the explanation of wetting behavior of pentane films on water requires the invoking of additional forces



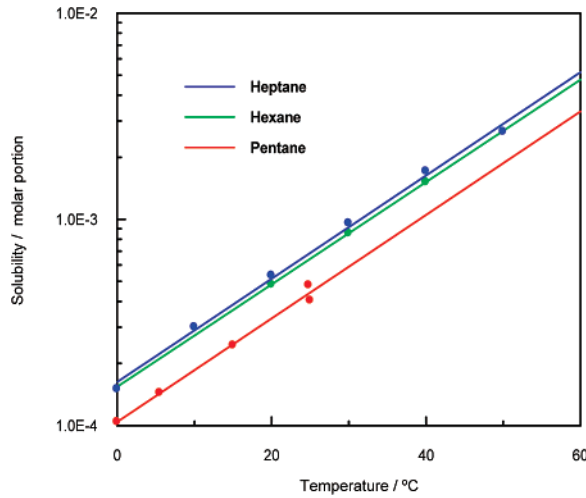
**Figure 4.** Isotherms of molecular component of the disjoining pressure calculated on the basis of eq 5 for the thick films region; the numbers at the lines indicate the temperature in °C.

to van der Waals mechanisms of surface forces. It seems reasonable to associate these additional forces with the solubility of water in pentane. In the literature, the latter is traditionally supposed to be negligible. In contrast, the analysis of the experimental solubility data (Figure 5) reveals that (1) while being restricted, the maximum concentration of water in low alkanes is not so small and is much higher than the solubility of alkane in water and (2) the solubility grows nearly exponentially with increase of temperature. Thus, the presence of water molecules in pentane has to be accounted for. The numerous experimental data on the stability of thin wetting films and interlayers of solutions with a nonpolar solvent and polar solute indicate the high responsivity of equilibrium thickness to the concentration of polar molecules.<sup>26–32</sup> The experiments point out that the most significant influence of solute on the stability of wetting films is observed in the range of diluted solutions. In the case under consideration, this influence is especially essential due to the fact that the interaction between the soluted water molecules and the water substrate leads to the specific adsorption. As a result, the additional surface forces appear, caused by the polarization of contacting phases in the electric field of dipoles of solute molecules. Several mechanisms of image-charge forces, associated to such polarization, have been considered in ref 33. The analysis showed that the contribution from polar molecules diffusely distributed across

**TABLE 1: The Values of Parameters Used for the Calculation of van der Waals Forces**

substance	$t, ^\circ\text{C}$	$\epsilon_0^{22}$	$\epsilon_\infty^{22}$	$C_{\text{MICRO}} = \epsilon_0 - \epsilon_\infty$	$\omega_{\text{MICRO}}^{22}$	$C_{\text{IR}} = \epsilon_\infty - 1 - C_{\text{UV}}$	$\omega_{\text{IR}}$	from Cauchy plot	
								$C_{\text{UV}}$	$\omega_{\text{UV}}$
water	20	80.21	5.6	74.61	$1.088 \times 10^{11}$	3.845	$9.70 \times 10^{13}$	0.755	$1.905 \times 10^{16}$
	25	78.36	5.2	73.16	$1.088 \times 10^{11}$	3.446	$9.70 \times 10^{13}$	0.754	$1.897 \times 10^{16}$
	30	76.56	5.2	71.36	$1.088 \times 10^{11}$	3.448	$9.70 \times 10^{13}$	0.752	$1.906 \times 10^{16}$
	40	73.18	3.9	69.28	$1.687 \times 10^{11}$	2.151	$9.70 \times 10^{13}$	0.749	$1.907 \times 10^{16}$
	50	69.89	4.0	65.89	$2.160 \times 10^{11}$	2.255	$9.70 \times 10^{13}$	0.745	$1.908 \times 10^{16}$
	60	66.70	4.2	62.50	$2.160 \times 10^{11}$	2.460	$9.70 \times 10^{13}$	0.740	$1.909 \times 10^{16}$
pentane	20	1.8433				0.0225	$5.54 \times 10^{14}$	0.8208	$1.882 \times 10^{16}$
	25	1.8356				0.0226	$5.54 \times 10^{14}$	0.8130	$1.884 \times 10^{16}$
	30	1.8279				0.0227	$5.54 \times 10^{14}$	0.8052	$1.887 \times 10^{16}$
	40	1.8124				0.0227	$5.54 \times 10^{14}$	0.7897	$1.892 \times 10^{16}$
	50	1.7970				0.0227	$5.54 \times 10^{14}$	0.7743	$1.897 \times 10^{16}$
	60	1.7820				0.0230	$5.54 \times 10^{14}$	0.7590	$1.903 \times 10^{16}$





**Figure 5.** Solubility of water in pentane,<sup>23,24</sup> hexane,<sup>23,24</sup> and heptane:<sup>25</sup> points, experimental data; solid lines, the least-squares exponential fits.

**TABLE 2: The Calculated Values of van der Waals Interaction Constants in the System**

temp, °C	$A_{132}$ , J	$A_{w1}$ , J m <sup>3</sup>	$A_{w2}$ , J m <sup>3</sup>
20	$1.06 \times 10^{-21}$	$9.75 \times 10^{-52}$	$7.82 \times 10^{-51}$
25	$8.72 \times 10^{-22}$	$6.96 \times 10^{-52}$	$7.86 \times 10^{-51}$
30	$5.94 \times 10^{-22}$	$2.01 \times 10^{-52}$	$7.92 \times 10^{-51}$
40	$2.13 \times 10^{-22}$	$-3.41 \times 10^{-52}$	$8.02 \times 10^{-51}$
50	$-1.45 \times 10^{-22}$	$-1.04 \times 10^{-51}$	$8.20 \times 10^{-51}$
60	$-4.50 \times 10^{-22}$	$-1.63 \times 10^{-51}$	$8.39 \times 10^{-51}$

liquid interlayer at low concentrations is relatively weak and hardly affects the film stability. The correlation interaction between layers adsorbed on the opposite interfaces is also not very essential for nonsymmetric systems like wetting films. At the same time, the appreciable force might arise due to the interaction of polar molecules in the adsorbed layer with their images in confining phases. In the case of high energy of specific adsorption, like hydrogen bonding considered in this paper, the strong force emerges even for diluted solutions.<sup>33–35</sup> It was shown also that the magnitude of image-charge forces strongly depends on the orientation of dipole moment of adsorbed molecule. Molecular dynamic simulation of a water–hydrocarbon system<sup>36</sup> established that closer to the hydrocarbon surface, water molecules being inside the water phase preferentially align their O–H bonds normally to the interface. On the basis of these results, it was physically reasonable to assume that the water molecules adsorbed at the interface from the pentane phase have the orientation favoring the hydrogen bonding with one O–H bond normal to the interface. In that case the total dipole moment of water molecule forms the angle of about 52.23° (that is, half of internal H–O–H angle) with the normal to the interface. For the convenience of further calculations this dipole moment will be decomposed on two constituents, normal and parallel to the phase boundary.

The contribution to the disjoining pressure, associated to the interaction of polar molecules in the adsorbed layer with their images in confining phases might be computed as<sup>33–35</sup>

$$\Pi_{\text{im}} = -\frac{d\Gamma^{(23)}}{dh}(U_{\text{im}}^{\text{n}} + U_{\text{im}}^{\text{p}} + U_{\text{lat}}) - \frac{d(U_{\text{im}}^{\text{n}} + U_{\text{im}}^{\text{p}} + U_{\text{lat}})}{dh}\Gamma^{(23)} \quad (9)$$

where  $\Gamma^{(23)}$  is the amount of water adsorbed at the pentane–water interface from the pentane phase,  $U_{\text{im}}^{\text{n}}$  and  $U_{\text{im}}^{\text{p}}$  are the potential electric energy of dipole oriented, respectively, normally and parallel to the interface in the field of its images, and  $U_{\text{lat}}$  is associated to lateral interaction inside the adsorption monolayer and is determined as the potential energy of dipole in the electric fields of adsorbed monolayer and image monolayers. For calculation of monolayer adsorption, it is expedient to use the Langmuir type isotherm with adsorption potential  $G_{\text{a}}$  determined by combined action of hydrogen bonding  $U_{\text{OH}}$ , van der Waals interaction  $U_{\text{m}}$  between the adsorbed molecule and the substrate (bulk water), image charge, and lateral interactions

$$\Gamma = \frac{\Gamma_0 b x}{1 + b x} \quad (10)$$

$$b = \exp\left(\frac{-G_{\text{a}}}{k_{\text{B}}T}\right) = \exp\left(-\frac{U_{\text{m}} + U_{\text{OH}} + U_{\text{im}}^{\text{n}} + U_{\text{im}}^{\text{p}} + U_{\text{lat}}}{k_{\text{B}}T}\right) \quad (11)$$

Here, as it was shown in refs 33–35

$$U_{\text{im}}^{\text{n}} = -\frac{(p^{\text{n}})^2}{4\epsilon_{30}} \sum_{k=0}^{\infty} \left\{ 2 \frac{(\beta_{32}\beta_{31})^{k+1}}{((k+1)h)^3} - \frac{\beta_{31}(\beta_{32}\beta_{31})^k}{((k+1)h - \delta)^3} - \frac{\beta_{32}(\beta_{32}\beta_{31})^k}{(kh + \delta)^3} \right\} \quad (12a)$$

$$U_{\text{im}}^{\text{p}} = \frac{(p^{\text{p}})^2}{8\epsilon_{30}} \sum_{k=0}^{\infty} \left\{ 2 \frac{(\beta_{32}\beta_{31})^{k+1}}{((k+1)h)^3} + \frac{\beta_{31}(\beta_{32}\beta_{31})^k}{((k+1)h - \delta)^3} + \frac{\beta_{32}(\beta_{32}\beta_{31})^k}{(kh + \delta)^3} \right\} \quad (12b)$$

$$U_{\text{lat}} = \frac{4(p^{\text{n}})^2}{\epsilon_{30}} \sum_{k=0}^{\infty} \left\{ \frac{(\beta_{32}\beta_{31})^k}{[\rho_0^2 + (2kh)^2]^{3/2}} - \frac{2(p^{\text{n}})^2}{\epsilon_{30}} \sum_{k=0}^{\infty} \left\{ \frac{\beta_{31}(\beta_{32}\beta_{31})^k}{[\rho_0^2 + (2(k+1)h - 2\delta)^2]^{3/2}} + \frac{\beta_{32}(\beta_{32}\beta_{31})^k}{[\rho_0^2 + (2kh + 2\delta)^2]^{3/2}} \right\} \right\} \quad (12c)$$

where  $\beta_{ij} = (\epsilon_{i0} - \epsilon_{j0})/(\epsilon_{i0} + \epsilon_{j0})$ ,  $p^{\text{n}}$  and  $p^{\text{p}}$  are normal and parallel to the phase boundary constituents of dipole moment of water molecule,  $\pi\rho_0^2$  is the area per dipole in the adsorption layer (dependent on the surface coverage  $\Gamma/\Gamma_0$ ),  $\delta$  is the minimum distance between the adsorbed dipole molecule and the interface,  $\Gamma_0$  is the number of adsorption places per unit of interfacial area, which was accepted, following ref 36, to be equal to 7.1 nm<sup>-2</sup>, and  $x$  is a molar portion of water solution in pentane. The double prime at the summation sign in eq 12c means that the term with  $k = 0$  is taken with a half weight. As regards the  $U_{\text{m}}$ , we have calculated it in the nonretarded limit on the basis of macroscopic approach, developed in ref 37. Then for the energy of van der Waals interaction,  $U_{\text{mwj}}$ , between the adsorbed water molecule and the phase  $j$ , confining liquid film, the following equation is valid<sup>13,38</sup>

$$U_{\text{mwj}}(z) = \frac{-3k_{\text{B}}T\nu_{\text{m}}}{8\pi z^3} \sum_{N=0}^{\infty} \frac{\epsilon_{\text{w}}(i\xi_N) - \epsilon_3(i\xi_N)}{\epsilon_{\text{w}}(i\xi_N) + 2\epsilon_3(i\xi_N)} \frac{\epsilon_j(i\xi_N) - \epsilon_3(i\xi_N)}{\epsilon_j(i\xi_N) + \epsilon_3(i\xi_N)} = -\frac{A_{\text{wj}}}{z^3} \quad (13)$$

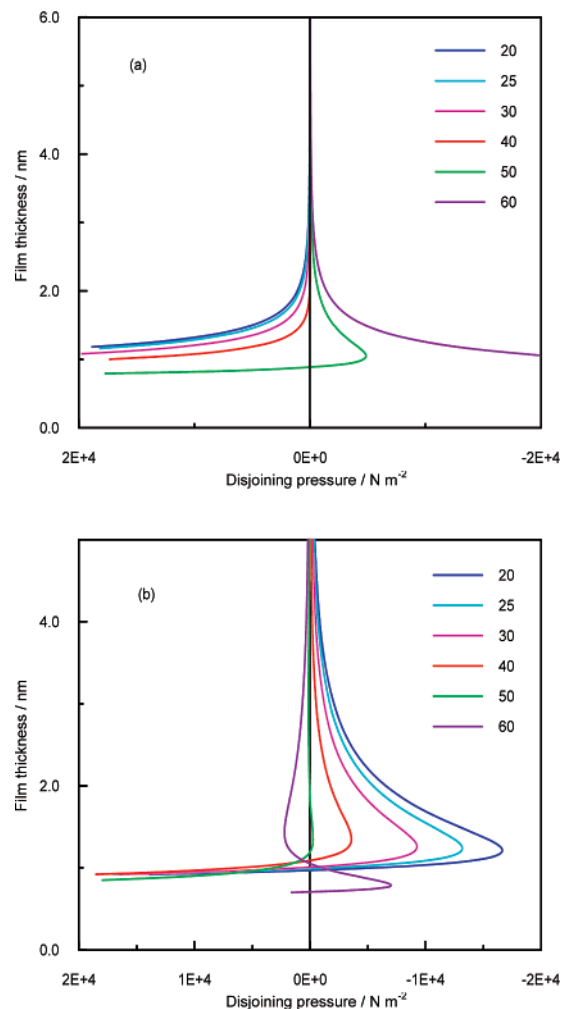
Here  $z$  is the distance between adsorbed molecule and confining phase  $j$ ,  $\nu_{\text{m}}$  is the molecular volume,  $A_{\text{wj}}$  is the Hamaker constant. The values of different constituents of adsorption energy calculated on the basis of eqs 12 and 13 at 20 °C are listed in Table 3. It is necessary to note that although the magnitude of adsorption, according to eq 10, is determined mainly by the energy of hydrogen bond, the image charge contribution to the disjoining pressure is less sensitive to it. This is related to the fact that the disjoining pressure is dictated by the behavior of the derivatives of the adsorption and electrostatic energy of adsorbed molecules in the image charge field and the field of lateral interaction over the film thickness (eq 9) and hence depends on  $U_{\text{OH}}$  only through the value of  $\Gamma$ . In agreement with previously reported analysis of magnitudes of adsorption at the opposite sides of wetting films<sup>34,35</sup> in the case of water soluted in pentane wetting films on water substrate, the value of  $\Gamma^{(23)}$  turns out to be more than 3 orders of magnitude greater than the adsorption of water on the pentane–air interface  $\Gamma^{(13)}$ . Therefore we have neglected in our calculations by the image-charge contribution into the disjoining pressure from monolayer, adsorbed at 1–3 interface.

The computed isotherms of image charge contribution and of total disjoining pressure including van der Waals and image charge components are presented in Figure 6. The analysis of above data indicates the following important features of the isotherms of disjoining pressure. The image charge contribution can be either attractive or repulsive depending on the sign and magnitude of van der Waals interaction between solute molecules and phase 1, opposite to the layer adsorbed at the 2–3 interface (see eqs 49 and 58 of ref 33). Thus the shift of  $A_{\text{w1}}$  into the negative region upon increasing the temperature causes the simultaneous appearance of a negative branch in the image charge contribution to disjoining pressure (Figure 6a). Further increasing the absolute value of  $A_{\text{w1}}$  provides the expanding of the range of thicknesses, corresponding to negative values of  $\Pi_{\text{im}}$  (cf. Table 2 and Figure 6a). Although the image forces decay much faster with increasing the film thickness and can be considered as short ranged in comparison to van der Waals forces, their influence on wetting behavior of pentane films on water substrate is crucial. Namely, at  $T = 20, 25, 30$ , and  $40$  °C, when van der Waals attraction prevents the film stability, the repulsive image charge forces provide the equilibrium between unsaturated vapor and wetting film. It is interesting to note that at  $T = 50$  °C both the van der Waals and the image charge interactions stabilize the wetting films at positive disjoining pressures, whereas at  $T = 60$  °C we again have the competition between the two contributions, but now the image charge attraction is dominated by the van der Waals repulsion.

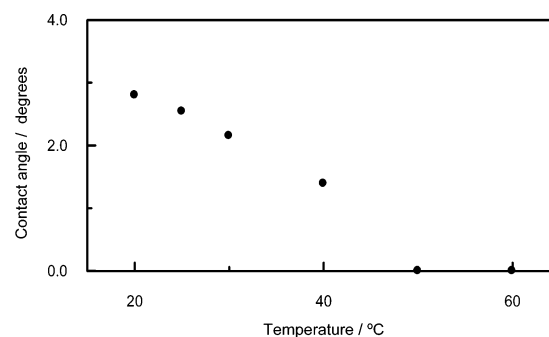
The temperature evolution of equilibrium contact angles calculated using eq 3 on the basis of total isotherms of the disjoining pressure is presented in Figure 7. According to this dependence the transition from partial (equilibrium between

**TABLE 3: The Different Contributions to the Adsorption Potential of Water Molecule at the Water/Pentane Interface in 1 nm Thick Pentane Film at 20 °C**

$U_{\text{OH}}/k_{\text{B}}T$	$U_{\text{mw2}}/k_{\text{B}}T$	$U_{\text{lat}}/k_{\text{B}}T$	$U_{\text{im}}^{\text{n}}/k_{\text{B}}T$	$U_{\text{im}}^{\text{p}}/k_{\text{B}}T$
−8.60	−0.11	−1.27	0.23	0.19



**Figure 6.** Isotherms of image charge contribution (a) and of total disjoining pressure (b) for pentane films on water surface at different temperatures.



**Figure 7.** Temperature dependence of contact angle for pentane on water.

liquid lens and wetting film) to complete wetting takes place at nearly 48 °C. This value shows to be in a good agreement with experimental findings (see Figure 1 in ref 5). As for the magnitudes of calculated contact angles, we did not find the experimentally measured values at different temperatures except for  $T = 24$  °C.<sup>4</sup> For that temperature Del Cerro and Jameson<sup>4</sup> have found that spreading of pentane along the water surface is accomplished by coexistence of very flat islands with wetting films, so the contact angle is close to zero. Our calculations give the value of contact angle  $\theta = 2.54^\circ$  in agreement with experimental observations. In contrast, should the van der Waals interaction be the only forces determining the wettability in above system, the value of the contact angle was about  $18^\circ$ .

## 5. Conclusions

It is shown in this paper that the peculiarities of wetting behavior and its temperature evolution of pentane on the top of water substrate can be considered as a result of joint action of two mechanisms of surface forces—van der Waals and image charge interactions. The analysis of the temperature influence on the magnitude of van der Waals forces based on the exact DLP equations and use of the detailed presentation of dielectric permittivity spectra of contacting phases showed that van der Waals forces alone can account neither for the experimentally observed equilibrium between pentane wetting film and pentane drop nor for the equilibrium of thin pentane films (less than 5 nm) with unsaturated vapor. At the same time the invoking of an additional—image-charge—mechanism, which takes into account the solubility of water in pentane and is related to the interaction of dipoles of water molecules in the adsorbed layer with their images in confining phases provides the detailed descriptions of all types of equilibrium and evolution of the contact angle with increasing the temperature.

**Acknowledgment.** The financial support of the Russian Foundation for Basic Research (Grant 06-08-00488) is gratefully acknowledged.

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