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Van der Waals interactions in multicomponent homogeneous thin films

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With 2 figures

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There is some uncertainty when calculating the disjoining pressure Π in thin plane-parallel films (thin film ≡ phase 2 with thickness h, sandwiched between two semi-infinite phases 1 and 3) from the macroscopic Lifshitz theory due to the lack of full information about the dependence of the dielectric susceptibility $\varepsilon(i\xi)$ on imaginary frequency $i\xi$ in the range $0 \leq \xi < \infty$ (1) (such data are available only for a given number of pure substances in a limited frequency range). For multicomponent films additional difficulties arise, first because one has to know $\varepsilon(i\xi)$ of the mixture (at different concentrations) and second because the concentration in the film and hence – $\varepsilon(i\xi)$ are functions of the co-ordinate normal to the film surfaces. Since the latter effect can be neglected for small concentrations and relatively thick films (2), now we shall consider only the case of a homogeneous two-component (components A and B) film bounded by the pure phases 1 and 3.

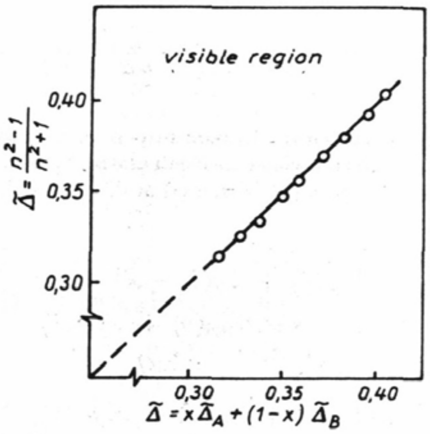

Fig. 1. $\tilde{\Delta}$ – values for the hexane-nitrobenzene mixture (ordinate) compared with those calculated by means of the combination rule [2] (abscissa) at $0{,}1 \leq x \leq 0{,}9$

Recently we showed (3) that the empirical formula proposed by *Krupp* (4)

$$\tilde{\Delta} = \frac{\varepsilon(i\xi) - 1}{\varepsilon(i\xi) + 1} = a.e^{-b\,\xi} \qquad [1]$$

($a = (n^2 - 1)/(n^2 + 1)$, n – refractive index at sodium light, b – constant) allows representing $\varepsilon(i\xi)$ for one component substances in the entire frequency range (for non-polar substances Eq. [1] holds at $\xi \geq 0$, for polar ones and room temperature – at $\xi > 2{,}4 \cdot 10^{14}$ rad/s (5)). By means of Eq. [1] we were able to derive a relatively simple analytical expression for Π in one-component films (3). Here we propose a combining rule for obtaining $\varepsilon(i\xi)$ of a two-component mixture from spectral data of the pure components. We use the formal similarity between the analytical expression for $\tilde{\Delta}$ and the molecular refraction (6). Since for a mixture of substances with nearly equal molecular volumes the molecular refraction of the mixture can be expressed as a sum of terms proportional to the concentrations and the molecular refractions of the pure components (6), we shall assume that such an additivity is valid for the quantity $\tilde{\Delta}$ of the mixture too:

$$\begin{aligned}\tilde{\Delta} &= x\tilde{\Delta}_A + (1 - x)\tilde{\Delta}_B \\ &= x a_A e^{-b_A\,\xi} + (1 - x) a_B e^{-b_B\,\xi}\,. \end{aligned} \qquad [2]$$

Here x is molar fraction of the component A and the subscripts denote that the respective quantities refer to the pure components. Eq. [2] can be tested in the visible region ($\varepsilon = n^2$) on the base of experimental data for n and at $\xi \geq 1 \cdot 10^{17}$ rad/s by means of the plasma formula (7): $\varepsilon(i\xi) = 1 + 3{,}18 \cdot 10^9\, N_e/\xi^2$ (N_e is number of electrons per cm^3). In figures 1 and 2 this is done for the hexane-nitrobenzene mixture. In figure 1 Δ, Δ_A and Δ_B are calculated using the experimental values (8) of the refractive indexes n, n_A and n_B of the mixture and the pure components respectively. The results for $\xi = 1 \cdot 10^{17}$ rad/s are plotted in figure 2; the values of N_e for the mixture and the pure components are calculated from density data. The $\tilde{\Delta}$-values for the mixture (plotted on the ordinate) coincide very well with the values calculated by means of the combination rule [2] (plotted on the abscissa) at $0{,}1 \leq x \leq 0{,}9$. These results confirm the possibility to calculate $\varepsilon(i\xi)$ of the mixture from Eqs. [1, 2]:

$$\varepsilon(i\xi) = \frac{1 + x a_A e^{-b_A\,\xi} + (1 - x) a_B e^{-b_B\,\xi}}{1 - x a_A e^{-b_A\,\xi} - (1 - x) a_B e^{-b_B\,\xi}}\,. \qquad [3]$$

Making use of Eq. [3] and the procedure described previously (3) the following approximate equation is obtained in the case of non-polar phases 1, 2 and 3:

$$\Pi = -\frac{A^*(h)}{6\pi h^3}\,, \qquad [4]$$

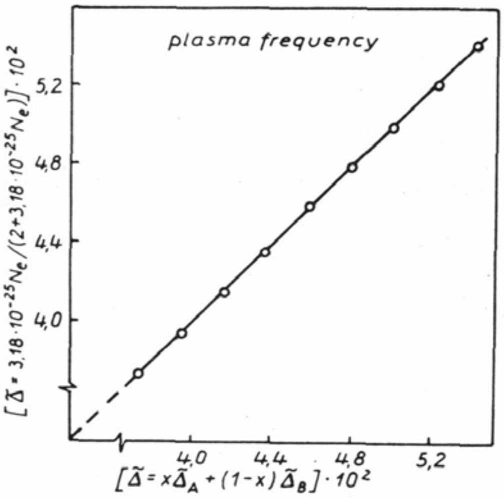

Fig. 2. $\tilde{\Delta}$ – values for the hexane-nitrobenzene mixture (ordinate) compared with those calculated by means of the combination rule [2] (abscissa) at $0{,}1 \leq x \leq 0{,}9$

$$\begin{aligned} A^*(b) &= x^2 \overset{*}{A}_{AA}(b) + 2x(1-x)\overset{*}{A}_{AB}(b) \\ &+ (1-x)^2 \overset{*}{A}_{BB}(b) + \overset{*}{A}_{13}(b) \\ &- x[\overset{*}{A}_{A1}(b) + \overset{*}{A}_{A3}(b)] \\ &- (1-x)[\overset{*}{A}_{B1}(b) + \overset{*}{A}_{B3}(b)], \qquad [5] \end{aligned}$$

where

$$\begin{aligned} \overset{*}{A}_{IJ}(b) &= \frac{3\hbar}{4\pi} \frac{a_I a_J}{b_I + b_J} \\ &\left[1 - \left(\frac{Db}{b_I + b_J + Db}\right)^3\right]; \\ I, J &= A, B, 1, 3; \end{aligned}$$

$2\pi\hbar$ is Planck's constant, $D = 2\overline{\varepsilon_2^{1/2}}/c$, c – velocity of light in vacuo, $\overline{\varepsilon_2^{1/2}} = \frac{1}{2}(n_2 + 1)$. When polar substances are considered a term $A_{n=0}$ depending only on the static dielectric constants of the phases 1, 2 and 3 has to be added to $A^*(b)$ (9).

It is worth noting that the same result can be derived using the effective additive intermolecular potential proposed in reference (10):

$$\begin{aligned} u_{IJ} &= -\frac{3\hbar}{R^6} \frac{a_I a_J}{4\pi^3 N_I N_J (b_I + b_J)} \\ &\left[1 - \left(\frac{DR}{b_I + b_J + DR}\right)^5\right] \qquad [6] \end{aligned}$$

(N_I is the number density of the respective pure substance, $R =$ the distance between the molecules). This formula describes the interactions of identical or different molecules I and J and accounts for the electromagnetic retardation in a dense medium (characterized by D). After substituting Eq. [6] in the microscopic formulae (11) for Π in a two-component film we obtain again the result given by Eqs. [4, 5]. Thus the applicability of Eq. [6] when considering dense mixtures is corroborated.

This fact is important, because with the intermolecular potential [6] the flexibility of the microscopic approach can be combined with the possibility given by Lifshitz theory to account for the influence of the medium and the electromagnetic retardation. In this way the effects of inhomogeneity in Π can be studied in a more selfconsistent manner (12).

Note added in proof:

Initially (3) the constant b in Eq. [1] was determined graphically in the plot $\ln \tilde{\Delta}$ against ξ. From the conditions that the straight line in this plot must pass through $\ln a = \ln[(n^2 - 1)/(n^2 + 1)]$ at $\xi = 0$ and must be tangent to the curve at frequencies where the plasma formula holds, the following expression for b is obtained: $b = 2\sqrt{2a}/e\omega_p$, e – logarithmic constant, $\omega_p = \sqrt{3{,}18 . 10^9\, N_e}$.

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