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Some effects of long range forces on interfacial phenomena

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Résumé. — Il existe des situations où la théorie classique des interfaces (avec un terme $(\nabla\rho)^2$ dans l'énergie libre) est qualitativement fautive, à cause de la longue portée des forces de Van der Waals. 1) La queue du profil de densité du côté gaz d'un interface gaz/liquide n'est pas exponentielle mais plutôt $\sim z^{-3}$ (où z est la distance au point milieu). 2) Dans l'expérience de Moldover et Cahn, l'épaisseur de la couche mouillante d'un liquide (b) entre deux autres liquides (a) et (c) peut être contrôlée par les forces à longue distance, plutôt que par la répulsion exponentielle entre parois qui se déduit de la théorie classique.

Abstract. — The conventional theory of interfaces (with a free energy term $\sim (\nabla\rho)^2$ where ρ is the appropriate density) may be qualitatively incorrect, because of long range effects associated with Van der Waals forces. 1) The tail of the density profile on the gas side of a liquid gas interface is not exponential (as usually predicted) but is $\sim z^{-3}$ (where z is the distance from the midpoint). 2) In the Moldover Cahn experiment, the thickness of the wetting layer of a liquid (b) between two other liquids (a) and (c) can be controlled by long range forces, not by the exponential repulsion between two interfaces which is derived from the conventional theory.

1. **Non exponential tails.** — The traditional approach for the density profiles $\rho(z)$ at a liquid gas interface [1-4] is based on the minimization of a functional :

$$\gamma = \int dz \left[F(\rho) - \mu\rho + p + \frac{1}{2} L \left(\frac{d\rho}{dz} \right)^2 \right] \quad (1)$$

where $F(\rho)$ is the free energy per cm^3 for a bulk fluid of density ρ , μ is the chemical potential, p the pressure, and L is assumed to be constant. In more refined versions of the theory, L is allowed to depend on ρ , and is related to a direct correlation function $C(\mathbf{r})$ [5] :

$$L = kT/6 \int C(\mathbf{r}) r^2 d\mathbf{r}. \quad (2)$$

For long range interactions $\sim r^{-6}$ this integral converges peacefully.

The description based on L leads to a density profile with *exponential tails* (in the gas phase and in the liquid phase) : this holds even if L has a (smooth) dependence on ρ . However, these tails are an artefact. Consider for instance the gas side of the interface ($z > 0$) at distances z from the Gibbs surface which are larger than the interface thickness e . In this region the effective $V(z)$ seen by one particle is obtained simply by integrating long range contributions from

a half space $z < 0$ filled with liquid (density ρ_L) ⁽¹⁾. With a pair interaction :

$$U(r_{ij}) = -4 \varepsilon \left(\frac{\sigma}{r_{ij}} \right)^6 \quad (r_{ij} \gg \sigma) \quad (3)$$

one arrives at a potential :

$$V(z) = -\frac{Q\rho_L}{z^3} \quad (z \gg e) \quad (4)$$

where

$$Q = (4\pi/3) \varepsilon \sigma^6.$$

Since the gas is perfect ($\rho_G \ll \rho_L$) we may write :

$$\begin{aligned} \rho(z)/\rho_G &= \exp(-V(z)/kT) \cong 1 - V(z)/kT \\ \frac{\rho(z) - \rho_G}{\rho_G} &= \frac{Q\rho_L}{kT} \frac{1}{z^3} \cong \left(\frac{\sigma}{z} \right)^3. \end{aligned} \quad (5)$$

In principle these deviations from the standard profile could be studied though the optical reflectance [6],

⁽¹⁾ We restrict our attention to situations far from the critical point : the gas density ρ_G is much smaller than ρ_L , and the contributions to $V(z)$ from molecules in the gas are negligible.

but these experiments work only near the critical point, and there the condition $z > e$ reduces the effect ⁽²⁾.

2. Thickness of wetting layers. — Other manifestations of long range forces may occur whenever two interfaces are close to one another. Here, as an example, let us consider the beautiful experiment of Moldover and Cahn [7] with three liquids a, b, c in coexistence (Fig. 1). We assume that b wets the ac interface, but also that the density of b is highest.

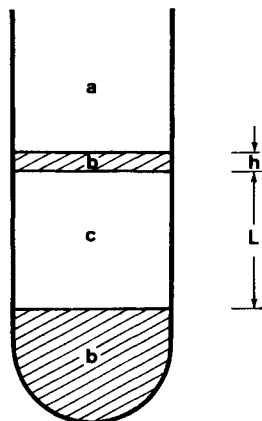


Fig. 1. — The Moldover Cahn experiment : the interface between a (air) and c (cyclohexane) is wetted by a third liquid b (methanol).

A complete discussion of the ac interface (with a wetting layer of b), within the classical theory, is given in reference [8]. It may be summarized in terms of an interfacial tension :

$$\gamma_{a,b,c} = \gamma_{ab} + \gamma_{bc} + \gamma' \exp(-h/e) + gLh(\rho_b - \rho_c) \quad (6)$$

where h is the thickness of the b layer, e is the thickness of a single interface (we take $e_{ab} = e_{bc} = e$ for simplicity), $g = 981 \text{ cm/s}^2$ is the gravitational acceleration, L is the altitude of the a(b) c interface with respect to the upper surface of the b liquid. The first two terms in (6) are standard interfacial tensions, the third term describes a repulsion between the two interfaces, and is directly related to the overlap between the « tails » associated with the two profiles : in the conventional theory, both the tails and the interaction are exponential (for $h \gg e$). The last term in equation (6) describes the gravitational work required to create the wetting layer ($\rho_b - \rho_c = \tilde{\rho}$ being the relevant density difference).

⁽²⁾ Note added in proof : The first mention of the z^{-3} tail seems to be due to S. E. Christiansen. See I. Plesner, O. Platz, *J. Chem. Phys.* **48** (1968) 5361, footnote II. I am indebted to Prof. J. Rowlinson for this observation.

After minimization of (6) with respect to h one obtains

$$h = h_1 = e \ln \left| \frac{\gamma'}{eLg\tilde{\rho}} \right|. \quad (7)$$

Typically $L = 1 \text{ cm}$, $e = 10 \text{ \AA}$, $\tilde{\rho} = 0.1 \text{ g/cm}^3$ and $\gamma' = 10 \text{ ergs/cm}^2$. Then the ln is of order 14 : the wetting layer is thin and rather insensitive to L .

We propose here a modified form of equation (6), where we incorporate the long range interactions between molecules of (a, b, c) in the layer region : we take the interactions in the factorized form :

$$E = -\frac{1}{2} \int \alpha(r) \alpha(r') |r - r'|^{-6} dr dr' \quad (8)$$

(with a suitable cut off at short distance). Here α is proportional to a specific polarizability, and takes three values ($\alpha_a, \alpha_b, \alpha_c$) depending on the region considered.

The result is of the form :

$$E = E_{\text{bulk}} + A[\gamma_{ab} + \gamma_{bc} + \gamma_{lr}] \quad (9)$$

where E_{bulk} is the extensive part, A is the area of interface, and γ_{lr} is a long range correction :

$$\gamma_{lr} = -\frac{\pi}{12h^2} (\alpha_a - \alpha_b)(\alpha_c - \alpha_b) = \frac{W}{h^2}. \quad (10)$$

Note that W vanishes, as it should, when two adjacent phases become identical ($\alpha_a = \alpha_b$ or $\alpha_c = \alpha_b$). Also when $\alpha_a = \alpha_c = 0$, equation (10) reduces to a standard formula for thin films in a vacuum [9].

Let us assume now $\alpha_a = 0$ (as in the Moldover Cahn experiment) : then W is positive (repulsive) if $\alpha_c > \alpha_b$ and negative (attractive) if $\alpha_c < \alpha_b$.

2.1 REPULSIVE CASE. — For $W > 0$, we may replace (6) by :

$$\gamma = \gamma_{ab} + \gamma_{bc} + \frac{W}{h^2} + \tilde{\rho}gLh \quad (11)$$

and obtain :

$$h = h_2 = \left(\frac{2W}{\tilde{\rho}gL} \right)^{1/3}. \quad (12)$$

Taking $W = 5 \times 10^{-14} \text{ ergs}$, $\tilde{\rho} = 0.1 \text{ g/cm}^3$ and $L = 1 \text{ cm}$, we then get $h \sim 100 \text{ \AA}$. The orders of magnitude are not very different from equation (7) but the L dependence is stronger.

In equation (11), we omitted all direct interactions between the two interfaces. These interactions exist, and they may well be modified in form by the non exponential tails, discussed in section 1. However, the tails become negligible if the three fluids (a, b, c) are essentially immiscible (in equation (5), $\rho - \rho_G$ is proportional to ρ_G).

Then the exponential repulsion $\gamma' \exp(-h/e)$ holds, and can be added to equation (11). But for $h \gg e$ it will not dominate the balance of forces.

2.2 ATTRACTIVE CASE $W < 0$. — Here we must keep the γ' term, which gives the only force preventing collapse :

$$\gamma = \gamma_{ab} + \gamma_{bc} + \gamma' \exp(-h/e) - \frac{|W|}{h^2} + \tilde{\rho} g L h. \quad (13)$$

Depending on the numbers, the dominant attractive force may be either gravitational (if $h \gg h_2$) or Van der Waals (if $h \ll h_2$). In the first case, we recover the Widom result (Eq. (7)). In the second case we reach a slightly different prediction :

$$h = h_3 \sim e \ln \left(\frac{\gamma' e^2}{2|W|} \right) \quad (h_3 \ll h_2). \quad (14)$$

The thickness h will hopefully be measured in the future by ellipsometric methods, or by other optical means. But independently of all details, it is clear that the long range of the Van der Waals forces will play a significant role for the structure of wetting layers.

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References

- [1] VAN DER WAALS, J. D., *Z. Phys. Chem.* **13** (1894) 657.
- [2] ROCARD, Y., *J. Physique Radium* **4** (1933) 533. *C. R. Hebd. Séan. Acad. Sci. Paris* **197** (1933) 122.
- [3] CAHN, J., HILLIARD, J., *J. Chem. Phys.* **28** (1958) 258.
- [4] WIDOM, B., in *Phase transitions and critical phenomena*, C. Domb, M. Green, eds., (Academic Press, NY) 1972, 2, chap. 3.
- [5] EVANS, R., *Adv. Phys.* **28** (1979) 143.
- [6] GILMER, G., GILMORE, W., HUANG, J., WEBB, W., *Phys. Rev. Lett.* **14** (1965) 491.
- MEUNIER, J., *Comptes Rendus* (1981), in press.
- [7] MOLDOVER, M., CAHN, J., *Science* **207** (1980) 1073.
- [8] WIDOM, B., *J. Chem. Phys.* **68** (1978) 3878.
- [9] See for instance *Molecular forces* (North Holland, Amsterdam) 1967, the reviews by CASIMIR, LYKLEMA and OVERBEEK.