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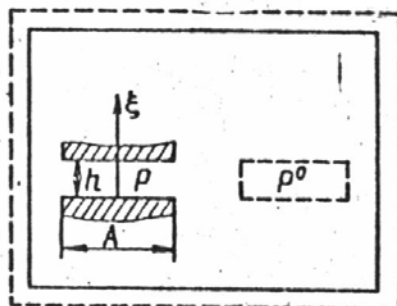
# ON THE STATISTICAL THERMODYNAMICS OF THIN FLUID FILMS

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Owing to intermolecular forces a thin plane-parallel film with thickness  $h$  is nonhomogeneous in direction perpendicular to its surfaces. Its mechanical equilibrium is described by the pressure tensor which has two components  $P_N$  and  $P_T$ . The film tension  $\Delta(h)$  is due to the difference between  $P_N=P$  and  $P_T$ . If the film is in equilibrium with a bulk phase with pressure  $P^0$  a difference  $\pi(h)=P-P^0$  called by Derjaguin disjoining pressure [1] may exist.

In the present paper virial expansions are obtained for the disjoining pressure, the film tension and the adsorption of one- and two-component films by means of the formalism of the grand canonical ensemble. The film is bounded by two rigid plates with area  $A$  creating an adsorption field immersed in a great thermostat containing gas with pressure  $P^0$  (fig. 1)\*. The first and the second virial coefficients of the disjoining pressure are calculated approximately using Sutherland's intermolecular potential. A possibility of simple calculation of  $\pi$  with more complicated intermolecular potentials is demonstrated.



The system shown in fig. 1 is a suitable model of adsorption in pores [3, 4]. On the other hand the method of the grand canonical ensemble may prove to be useful in the statistical thermodynamics of multicomponent liquid films. Russanov and Kuni, using functional expansions, were the first who treated this system [5, 6].

\*) Derjaguin and Martynov [2] have taken into account the film nonhomogeneity in the case when the gas is ideal.

Since the film is an open isothermal system its thermodynamic state is suitably described by the  $\Omega$ -potential. In that case the Gibbs' fundamental equation will read:

$$d\Omega = SdT + PdV - \Delta dA + \sum_i N_i d\mu_i \quad (1)$$

We choose as reference system (denoted by superscript zero) the same volume  $V = A \cdot h$  situated in the bulk phase. Then

$$d\Omega^0 = S^0 dT + P^0 dV + \sum_i N_i^0 d\mu_i^0 \quad (2)$$

In (1) and (2)  $T$  is temperature,  $S$  – entropy,  $N_i$  and  $\mu_i$  are the number of molecules and the chemical potential of the  $i$ -th component.

Since at equilibrium

$$\mu_i = \mu_i^0 \quad (3)$$

and

$$P - P^0 = \pi \quad (4)$$

from (1) and (2) it follows:

$$d\tilde{\Omega} = SdT + \pi A dh - \Delta dA + \sum_i I_i A d\mu_i \quad (5)$$

where  $\tilde{\Omega}$  and  $\tilde{S}$  are Gibbs' excess functions of the  $\Omega$ -potential and the entropy respectively;  $I_i = \tilde{N}_i / A = (N_i - N_i^0) / A$  is the adsorption of the  $i$ -th component with respect to the film as a whole.

By means of Euler's theorem from (5) we obtain

$$\tilde{\Omega} = \pi V - \Delta A \quad (6)$$

so that

$$\Delta = \pi h - \frac{\tilde{\Omega}}{A} \quad (7)$$

According to (5)

$$\pi = \left( \frac{\partial \tilde{\Omega}}{\partial V} \right)_{T, A, \mu_i} = \left( \frac{\partial \tilde{\Omega} / A}{\partial h} \right)_{T, A, \mu_i} \quad (8)$$

and

$$I_i = \frac{1}{A} \left( \frac{\partial \tilde{\Omega}}{\partial \mu_i} \right)_{T, V, A, \mu_j \neq i} = \left( \frac{\partial \tilde{\Omega} / A}{\partial \mu_i} \right)_{T, h, A, \mu_j \neq i} \quad (9)$$

The  $\Omega$ -potential can be expressed by the grand partition function  $\Xi$ .

If the gas is one-component [7]

$$\tilde{\Omega} = kT \ln \frac{\Xi}{\Xi^0} = kT \ln \sum_{N \geq 0} \frac{Z_N}{N!} z^N - kT \ln \sum_{N \geq 0} \frac{Z_N^0}{N!} z^0 \quad (10)$$

where  $Z_n$  are classical configuration integrals,  $z$  – activity and  $k$  – Boltzmann's constant.

Equation (10) can be rewritten in the form [7]

$$\tilde{\Omega} = kTV \sum_{i>1} (b_i - b_i^0) z^i \quad (11)$$

where

$$b_1 = Z_1/V \quad (12a)$$

$$b_2 = (Z_2 - Z_1^2)/2V \quad (12b)$$

and in  $b_i^0$  the respective  $Z^0$  stay for  $Z$ .

The activity  $z$  can be represented as power series of the number density  $\rho_0$  in the bulk phase [7]

$$z = \rho_0 - 2b_2^0 \rho_0^2 + (8b_2^0{}^2 - 3b_3^0) \rho_0^3 + \dots \quad (13)$$

By means of (11) and (13) the virial expansion of the  $\tilde{\Omega}$ -potential is derived:

$$\frac{\tilde{\Omega}}{A} = \sum_{i>1} B_i \rho_0^i, \quad (14)$$

where the virial coefficients have the form

$$B_1 = kT (b_1 - b_1^0) \quad (15a)$$

$$B_2 = kT [(b_2 - b_2^0) - 2b_2^0 (b_1 - b_1^0)] \quad (15b)$$

Combining (14) with (8), (7) and (9) we obtain

$$\pi = \sum_{i>1} \rho_0^i \frac{\partial B_i}{\partial h} \quad (16)$$

$$\Delta = \sum_{i>1} (h \frac{\partial B_i}{\partial h} - B_i) \rho_0^i \quad (17)$$

$$\Gamma = \frac{\partial}{\partial \mu} \left( \sum_{i>1} B_i \rho_0^i \right) \quad (18)$$

The last three equations yield the virial expansions for the disjoining pressure, the film tension and the adsorption in an one component film.

Now we shall calculate the first and the second virial coefficients of the disjoining pressure  $\partial B_1/\partial h$  and  $\partial B_2/\partial h$  making use of Sutherland's intermolecular potential

$$\begin{aligned}
 u_{12} & \rightarrow \infty & 0 < r < \delta \\
 u_{12} & = \frac{\beta_{AA}}{r^6} & \delta < r < \infty.
 \end{aligned}
 \tag{19}$$

For the interaction potential of one molecule of the film with both plates we can write [8]

$$u(\zeta) = -\frac{\pi \rho_s \beta_{AS}}{6} \left( \frac{1}{\zeta^3} + \frac{1}{(h-\zeta)^3} \right)
 \tag{20}$$

( $\zeta$  is the coordinate normal to the plates surfaces).

For the system considered here the first and the second configurational integrals have the form

$$Z_1 = \int_{(V)} \exp\left(-\frac{u_1}{kT}\right) dR_1
 \tag{21}$$

$$Z_2 = \int_{(V)} \int_{(V)} \exp\left(-\frac{u_1 + u_2 + u_{12}}{kT}\right) dR_1 dR_2
 \tag{22}$$

Assuming  $|u/kT| \ll 1$  and  $|u_{12}/kT| \ll 1$ , expanding the integrands in (21) and (22) in power series and retaining linear and square terms from (12), (15), (16), (19) and (20) we obtain\*

$$\pi = \frac{2K_{AS} - K_{AA}}{h^3} + \frac{\pi}{2} \frac{K_{AS}}{kT \delta^2} \frac{1}{h^4} (\beta_{AA} \rho_A - \beta_{AS} \rho_s),
 \tag{23}$$

where  $\rho_A = \rho_0$ ,  $K_{ij} = \pi \rho_i \rho_j \beta_{ij}/6$  (the approximation  $h \gg 2\delta$  has been used and the terms of higher order than  $h^{-4}$  have been neglected). The first term in the right hand side of eq. (23) exactly coincides with the result of the microscopic theory for a homogeneous film with number density  $\rho_0$  [9]. It takes into account the interactions of the gas molecules between themselves and that with both rigid plates. The second term is temperature dependent

\*) The plates are considered as being semiinfinite with density  $\rho_s$ ;  $\beta_{AA}$  and  $\beta_{AS}$  are the constants in London's intermolecular potential for gas-gas and gas-plate interactions respectively.

\*) In order to calculate the whole force acting on unit area of the plates we have to add to (24) a term  $-K_{SS}/h^3$  which allows for the attraction between the plates [9].

and is connected with the density changes in the film with respect to the bulk phase.

Eq. (23) would coincide with the asymptotic expression of the disjoining pressure of Kuni, Russarov and Brodskaja [4, 6] for the present model if there  $l_{\infty} = l(h \rightarrow \infty)$  is replaced by  $K_{AS}/kT\delta^2$ .

This value of  $l_{\infty}$  is derived from (18) if  $\rho_0 \ll \rho_s$  and  $|\mu_{\infty}(\delta)/kT| \ll 1$  ( $u_{\infty}(\delta)$  is the value of  $u$  at  $h \rightarrow \infty$  and  $\zeta = \delta$ ).

Eq. (23) could be obtained in a simpler manner by means of the virial expansion used in the present work if the virial coefficients  $B_{i>1}$  are put equal to zero and when calculating  $B_1$  from (15a), (12a) and (21) the potential  $u_1$  is represented as a sum of the external potential (20) due to the plates and the potential of an effective molecular field

$$u^*(\zeta) = \frac{\pi \rho_A \beta_{AA}}{12} \left[ \frac{1}{\zeta^3} + \frac{1}{(h-\zeta)^3} \right] \quad (24)$$

It takes into account the change of the energy of one molecule owing to its interactions with all other molecules in a hypothetical film with number density  $\rho_A = \rho_0$  (a uniform distribution of the molecules throughout the film volume is assumed). In that case  $\pi = (\partial B_1 / \partial h) \rho_0$  and the same result is obtained again under the condition  $\rho_0 \ll \rho_s$ .

The generalization of the theory for a film consisting of two components A and B is straightforward [7]. Now instead of (11) we must write

$$\tilde{\Omega} = kTV [(b_{10} - b_{10}^{\circ}) z_A + (b_{01} - b_{01}^{\circ}) z_B + (b_{20} - b_{20}^{\circ}) z_A^2 + (b_{02} - b_{02}^{\circ}) z_B^2 + (b_{11} - b_{11}^{\circ}) z_A z_B + \dots] \quad (25)$$

and instead of (13)

$$z_A = \rho_A^{\circ} - 2b_{20}^{\circ} \rho_A^{\circ 2} - b_{11}^{\circ} \rho_A^{\circ} \rho_B^{\circ} + \dots \quad (26a)$$

$$z_B = \rho_B^{\circ} - 2b_{02}^{\circ} \rho_B^{\circ 2} - b_{11}^{\circ} \rho_A^{\circ} \rho_B^{\circ} + \dots \quad (26b)$$

In these formulae  $b_{km}$  (and  $B_{km}$  - see (27)) refers to  $k$  molecules of type A and  $m$  molecules of type B.

Hence

$$\tilde{\Omega} = B_{10} \rho_A^{\circ} + B_{01} \rho_B^{\circ} + B_{20} \rho_A^{\circ 2} + B_{02} \rho_B^{\circ 2} + B_{11} \rho_A^{\circ} \rho_B^{\circ} + \dots \quad (27)$$

where  $B_{10}$ ,  $B_{01}$  coincide with the virial coefficient  $B_1$  and  $B_{20}$ ,  $B_{02}$  - with  $B_2$  (see (15a) and (15b)) and

$$B_{11} = hkT [(b_{11} - b_{11}^{\circ}) - b_{11}^{\circ}(b_{10}^{\circ} - b_{10}^{\circ}) - b_{11}^{\circ}(b_{01} - b_{01}^{\circ})] \quad (28)$$

The new coefficient  $B_{11}$ , due to the interaction of one molecule of type A with one molecule of type B, is calculated by the procedure described above. The corresponding formula for the disjoining pressure (16) reads (see footnote on p.5):

$$\begin{aligned} \pi &= \frac{\partial B_{10}}{\partial h} \rho_A^{\circ} + \frac{\partial B_{01}}{\partial h} \rho_B^{\circ} + \frac{\partial B_{20}}{\partial h} \rho_A^{\circ 2} + \frac{\partial B_{02}}{\partial h} \rho_B^{\circ 2} + \frac{\partial B_{11}}{\partial h} \rho_A^{\circ} \rho_B^{\circ} = \\ &= \frac{1}{h^3} (2K_{AS} + 2K_{BS} - K_{AA} - K_{BB} - 2K_{AB}) + \\ &+ \frac{\pi}{2} \frac{1}{kT \delta^2} \frac{1}{h^4} \left[ K_{AS} (\beta_{AA} \rho_A^{\circ} + \beta_{AB} \rho_B^{\circ} - \beta_{AS} \rho_s) + \right. \\ &\left. + K_{BS} (\beta_{BB} \rho_B^{\circ} + \beta_{AB} \rho_A^{\circ} - \beta_{BS} \rho_s) \right]. \end{aligned} \quad (29)$$

Eq. (29) coincides with the result of Russanov, Kuni and Brodskaja [6] when  $\rho_s \gg \rho_A^{\circ}$  and  $\rho_s \gg \rho_B^{\circ}$ .

Again, as in the case of one component film, the same result for  $\pi$  could be obtained in a simpler manner if in determining  $B_{10}$  and  $B_{01}$  the interactions between the gas molecules are accounted for through potentials of effective molecular fields and  $\pi = (\partial B_{10} / \partial h) \rho_A^{\circ} + (\partial B_{01} / \partial h) \rho_B^{\circ}$ . In that case the configurational integrals  $Z_{10}$  and  $Z_{01}$  are given by

$$Z_{km} = \int \exp \left\{ -\frac{X_{km}}{kT} \left[ \frac{1}{\zeta^3} + \frac{1}{(h-\zeta)^3} \right] \right\} dR \quad (30)$$

(V)

where  $X_{10} = \frac{\pi}{12} (\beta_{AA} \rho_A^{\circ} + \beta_{AB} \rho_B^{\circ} - \beta_{AS} \rho_s)$

$$X_{01} = \frac{\pi}{12} (\beta_{BB} \rho_B^{\circ} + \beta_{AB} \rho_A^{\circ} - \beta_{BS} \rho_s) .$$

The possibility of obtaining a correct result for  $\pi$  by calculating only first virial coefficients demonstrated above allows to make use of more realistic intermolecular potentials. This possibility will be illustrated with the following additive intermolecular potential [10]

$$u_{ij}(r) = -\frac{\beta_{ij}}{r^6} \left[ 1 - \left( \frac{Dr}{d_i + d_j + Dr} \right)^5 \right] \quad (31)$$

where the constants  $\beta_{ij}$ ,  $d$  and  $D$  can be determined from available spectral data [11]. Eq. (31) has been derived from the macroscopic Lifshitz theory and takes into account the electromagnetic retardation in a dense medium.

So making use of (31) we have to write

$$\frac{1}{\zeta^3} \left[ 1 - \left( \frac{D\zeta}{d_i + d_j + D\zeta} \right)^3 \right] + \frac{1}{(h-\zeta)^3} \left[ 1 - \left( \frac{S_i - D\zeta}{d_i + d_j + Dh - D\zeta} \right)^3 \right]$$

instead of  $1/\zeta^3 + 1/(h-\zeta)^3$  in eq. (30). The expression for  $\pi$  finally obtained in the same manner is given by eq. (29), where in the terms proportional to  $h^{-3}$  the  $K_{ij}$ 's ( $K_{AS}$ ,  $K_{BS}$  . . . .) are replaced by

$$K_{ij} \left[ 1 - \left( \frac{Dh}{d_i + d_j + Dh} \right)^3 \right] \quad \text{and in the terms}$$

proportional to  $h^{-4}$

$$K_{ij}\beta_{ik} \left[ 1 - \frac{1}{2} \left( \frac{Dh}{d_i + d_j + Dh} \right)^4 - \frac{1}{2} \left( \frac{Dh}{d_i + d_k + Dh} \right)^4 \right]$$

stay for  $K_{ij}\beta_{ik}$ .

In the cases considered here the contribution from gas-gas and gas-solid interactions as well as the temperature dependent term are immaterial with respect to the solid-solid attraction (see eq. (23)). The formalism of virial expansion limits the quantitative application of the results to films of dense fluids. The qualitative features however should be the same also in liquid films where the contribution from the temperature dependent absorptive term could be significant.

## Summary

The formalism of the grand canonical ensemble is applied to thin gas film. Virial expansions for disjoining pressure, film tension and adsorption are derived. The first and the second virial coefficients for the disjoining pressure are calculated with Sutherland's intermolecular potential. A possibility of simple calculation of the disjoining pressure including adsorptive effects is demonstrated with a more realistic intermolecular potential accounting for the electromagnetic retardation in dense medium.



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## Вопрос.

На каких расстояниях начинает проявляться влияние эффекта неоднородности газовой прослойки и в каком соответствии оно находится с силой молекулярного притяжения пластин?

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## Ответ.

Как я уже отметил эффект неоднородности газа, вообще говоря, очень мал. Может быть он станет существенным при толщинах порядка диаметра молекул, когда теория не применима. Поэтому численных оценок не было сделано. В растворах это может случиться и при больших толщинах, и когда теория для растворов будет закончена, приведем и соответствующие оценки.