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MODELLING OF LIQUID-VAPOUR INTERFACE. STUDY OF SURFACE TENSION AND HYDROSTATIC EQUILIBRIUM

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1. Modelling of the interface

The structure of liquid-vapour interfacial region can be studied by computer simulation or integral equation theories. In spite of appreciable efforts which were devoted to the study of correlation functions in the inhomogeneous region of liquids the details of the distributions are not yet known. In our laboratory we have succeeded in solving the Born-Green-Yvon-Bogolyubov equations for the liquid-rigid wall system /1/ and to some extent also for the liquid-vapour interface /2/.

In this work we report some numerical results about the dependence of the transverse and normal component of pressure tensor upon the form of the density profile and upon the pair correlation function. Harasima /3/ pointed out that within the approximation due to the Fowler model /4/ the excess of transverse pressure is exhibited as the compression $\Delta p_{x,y} > 0$ and not as a tension.

The components of the pressure tensor can be calculated in the following way:

$$p_i(z) = \rho(z)\, kT - \frac{1}{2} \int \frac{x_i^2}{r_i} V'(r)\, \rho(z_1) \rho(z_2)\, g(\vec{r}_1,\vec{r}_2)\, d\vec{r}_2 \qquad (1)$$

x_i refers to any of three Cartesian components of the radius vector between particles 1 and 2 (see Fig. 1). Let the Gibbs dividing surface coincide with the density discontinuity and thus $p_x(z)$ and $p_y(z)$ are identical and represent the components of transverse stress while $p_z(z)$ is a normal stress. The Lennard-Jones pair potential is denoted by $V(r)$, while $\rho(z)$ and $g(\vec{r}_1,\vec{r}_2)$ are the density profile and pair correlation function, respectively.

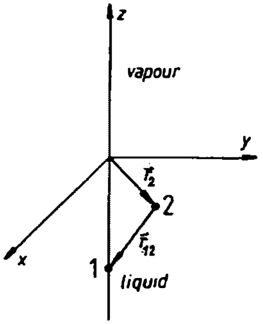


Fig. 1. The meaning of the geometrical symbols appearing in equation (1).

The surface tension can be expressed as the integral of the negative excess of the transverse component of the pressure tensor over z coordinate

$$\gamma = - \int (p_x(z) - p_b)\, dz \qquad (2)$$

where p_b is the bulk limit of the diagonal values of the pressure tensor and is equal to the isotropic value, which can be expressed in the following way

$$p_b = \rho kT - \frac{2\pi\rho}{3} \int r^3 V'(r)\, g(r)\, dr \qquad (3)$$

The simplest model of the interface is due to Fowler /4/. In this model it is supposed that the density profile has the form of a step function and that the pair correlation function is liquid-like up to the surface. The value of the surface tension in the Fowler model depends upon what is inserted for p_b in (2). If one inserts (3) or $p_z(z)$ one gets a negative, or a positive result, respectively.

The fact that two equally reasonable suppositions lead to results which differ in sign means that the model of discontinuous density profile involves a high degree of internal inconsistency This means that the supposition of step-like density profile is not appropriate and we introduce the following model for the density profile and pair correlation function:

$$\rho(z) = \rho_{vap} + 0.5\,(\rho_{liq} - \rho_{vap})\,\tanh\,(2z/l) \qquad (4)$$

$$g(\vec{r}_1,\vec{r}_2) = \alpha\,(\vec{r}_1,\vec{r}_2)\, g_{liq}(r_{12}) + (1 - \alpha\,(\vec{r}_1,\vec{r}_2))\, g_{vap}(r_{12}) \qquad (5)$$

where $\alpha\,(\vec{r}_1,\vec{r}_2)$ is a weighting function which was defined in terms of mean density $\bar{\rho} = (\rho\,(r_1) + \rho\,(r_2))/2$:

$$\alpha(\rho) = (\bar{\rho} - \rho_{vap})/(\rho_{liq} - \rho_{vap}) \qquad (6)$$

with ρ_{liq} and ρ_{vap} being the density of liquid and vapour, respectively and l is the width of the interface. $g_{liq}(r)$ was taken from Verlet's molecular dynamics results /5/.

Expressions (4) and (5) define our model for liquid-vapour interface uniquely. The Fowler model is characterized by $l = 0$ while the realistic value of the parameter l defining the thickness of the interface, as determined by computer simulation in the vicinity of the triple point /6/ is $l = 1.6\sigma$.

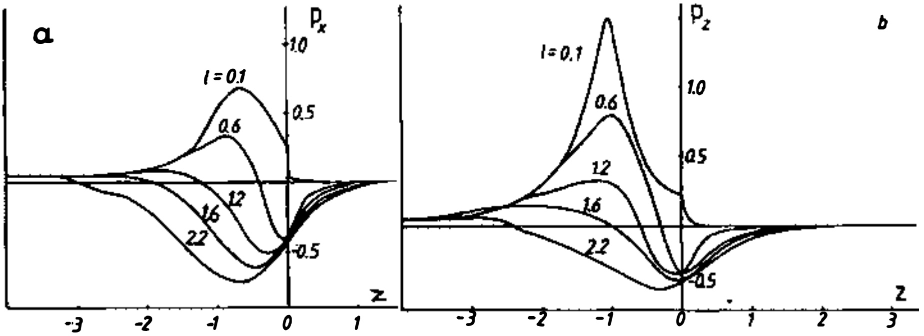


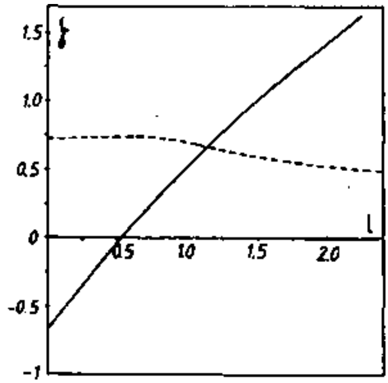
Fig. 2. The transverse (a) and normal (b) component of pressure tensor as a function of z coordinate calculated for various values of the interface thickness l.

2. Results and discussion

We evaluated the transverse and normal component of surface tension for several values of l. The results are depicted in Figure 2. We can see that the introduction of finite width of the liquid-vapour interface remedies the inconsistencies at $l = 0$. With increasing value of l the system approaches hydrostatic equilibrium which is exhibited by a weakening of the excess of normal component of pressure tensor. It is interesting to point out that the deviation from the hydrostatic equilibrium with the interface has its minimum between $l = 1.5\sigma$ and $l = 1.6\sigma$ This is in perfect agreement with the results of molecular dynamics simulation by Walton et al. /6/ who showed that close to the triple point ($\rho_{liq} = 0.797\ \sigma^{-3}$; $kT/\varepsilon = 0.723$) the surface thickness is equal to $l = 1.62\sigma$. We may, of course, not expect that such a simple model as we have introduced above would lead to a complete equilibration of the interface.

Figure 3 shows the integral expressing the surface tension according to (2) as a function of l. The full line corresponds to $p_b = p_x(-\infty)$ and the broken line to $p_b = p_z(z)$.

Fig. 3. The surface tension as calculated by means of eq. (2). Full line: Inserting $p_x(-\infty) = p_z(-\infty)$ for p_b; broken line $p_b = p_z(z)$.
The surface tension is given in units ε/σ^2.



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