A
MOLECULAR DYNAMICS INVESTIGATION OF A FREE SURFACE OF LIQUID ARGON

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ABSTRACT

A molecular dynamics simulation technique is employed to investigate the equilibrium molecular structure of the liquid - vapour interfacial region for argon at about I24 °K .

The density profile through the surface is found to be of a non-monotonic form.

The pair distribution function in the surface is also determined and compared to radial distribution functionsof the interior liquid. The surface tension and surface energy are also obtained and are found to be in agreement with generally accepted experimental values.

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SECTION I

Introduction

Computer simulation methods have in recent years played a role of increasing importance in liquid physics.

In a field, which is characterised by the difficulty, with which experimental information can be obtained on the microscopic level, Monte Carlo (MC) and Molecular Dynamics (MD) have provided the insight into the molecular structure of classical dense fluids, which has been essential for the further development of theoretical approaches.(1-7,46,47).In this, molecular dynamics has enjoyed a natural advantage over the MC method, because of its suitability for investigations of non-equilibrium systems.

Both types of simulation have, however, yielded results of such accuracy and consistency, that they have largely begun to fill the role, usually played by experiment : theoretical predictions often are in the first instance compared with simulation results, and approximative assumptions employed in theoretical derivations are assessed in the light of the detailed information provided by MD and MC calculations .(7,8,46-48)

One particular aspect of classical liquids, which however has to be excluded from this assessment, is that of the liquid surface. The use of computer simulation techniques to investigate the molecular structure of phase boundaries, encounters particular difficulties, which stem from the fact, that even with the most modern computers, direct simulation of of only a couple of thousand particles - at best - is possible. To simulate a system of macroscopic dimensions, one is thus forced to make use of the artifice of enclosing the finite number of molecules in a "cell", for which periodic boundary conditions are assumed.In so doing, an isotropy is implied in the model, which makes it difficult to deal with a situation as anisotropic as a liquid- vapour interface.

Phase boundaries have of course been simulated implicitely for so-called "micro-crystals", where MD calculations have been performed for small numbers of particles, without using periodic boundary conditions. A number of such simulations have been reported, right from the beginning of the MC and MD method, assuming various types of interactions, and mostly using a two-dimensional model (c.f. Cotterill et al.1973 (49), for a recent example), but these calculations do not seem suitable for gaining information on the macroscopic liquid surface.

It seems to be due to the above-mentioned difficulty posed by the anisotropy of the interface, that until now, no computer simulations appear to have been reported for the three-dimensional liquid .

The present work uses an apparently novel but very simple approach to overcome the anisotropy problem, for a molecular dynamics investigation of a plane liquid - vapour interface of argon. The investigation reported here, has been restricted to equilibrium properties.

We have divided this article into three parts :
In the remainder of Part I we will review the physics of the ("simple") liquid surface. This dicussion will mainly be in general and quantitative terms : the aim is, to outline the basic features of this field, and to provide a background for the present investigation in these terms.

Details of the methods and results reported, are reviewed in Part III , where the results of the present work are discussed.

Part II is concerned with the method used in this investigation.

SECTION 2

The Surface of Simple Liquids

The thermodynamical and statistical mechanical theories* of the liquid surface have, starting with the work of Gibbs(9), Guggenheim(10,10a) and Fowler(25),been well established for a long time on the phenomenological level. While the connection between the molecular structure of the surface, and the thermodynamic quantities like surface tension and surface energy, which are fairly easily accessible by experiment, is thus available, it has been found difficult to obtain information about the molecular structure itself.

The microscopic structure of a classical dense fluid is most suitably discussed in the mathematical framework of the configurational distribution functions.(48,50)

We can define the N-th order configurational distribution function $n^{(N)}(\underset{\sim}{r}_1,\underset{\sim}{r}_2,\cdots\underset{\sim}{r}_N)$ as the probability density of (the) N molecules having positions equal to $(\underset{\sim}{r}_1,\underset{\sim}{r}_2,\underset{\sim}{r}_3,\cdots\underset{\sim}{r}_N)$ normalised by

$$N! = \int\cdots\iint n^{(N)}(\underset{\sim}{r}_1\ \ \underset{\sim}{r}_N)\,d\underset{\sim}{r}_1\,d\underset{\sim}{r}_2\cdots d\underset{\sim}{r}_N \qquad -(2.1)$$

wher N is the number of particles of the (closed) system.

By integration over the "unwanted" coordinates, lower order distribution functions $n^{(h)}$ ($h \leq N$) can be obtain-

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* (9-26)

ed, in particular the pair distribution $\overset{(2)}{n}(\underset{\sim}{r}_1,\underset{\sim}{r}_2)$ for the probability of finding a pair of molecules, having positions at $\underset{\sim}{r}_1$ and $\underset{\sim}{r}_2$, and the singlet distribution, which is just the number distribution at point $\underset{\sim}{r}$.

These last two functions are of particicular importance, since, for a simple classical liquid, for which pairwise interactions between molecules are assumed, these functions alone determine the thermodynamic equilibrium quantities.

For the homogeneous interior of the liquid, $\overset{(1)}{n}(\underset{\sim}{r})$ equals a constant number density n ,and $\overset{(2)}{n}$ becomes a function of the scalar distance $r_{12} = |\underset{\sim}{r}_2 - \underset{\sim}{r}_1|$ between molecules only. We can therefore introduce the radial distribution function $\overset{(2)}{g}(r_{12})$ by writing

$$\overset{(2)}{n}(r_{12}) = n^2 \cdot \overset{(2)}{g}(r_{12}) \qquad -(2.2)$$

The pressure and the internal energy can then be expressed as*

$$P = nkT - \frac{n^2}{6}\int_0^\infty g^{(2)}(r) \cdot \frac{\partial \psi(r)}{\partial r} \cdot 4\pi r^3 dr \qquad -(2.3)$$

$$U = \frac{3NkT}{2} + \frac{n^2 V}{2}\int_0^\infty g^{(2)}(r)\,\psi(r) \cdot 4\pi r^2 dr \qquad -(2.4)$$

The main effort of equilibrium statistical mechanics for classical liquids, has therefore directed at obtaining the radial distribution function $\overset{(2)}{g}(r)$, generally

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* $\psi(r)$ is the interaction potential.

as numerical solutions of certain non-linear integral equations.

Comparison of these results with experimental information is then possible, either with values for thermodynamic quantities via equations like (2.3), or by comparison with radial distribution functions obtained from X-ray or neutron scattering experiments.
Some remaining difficulties characterizing this field, can be briefly summarized as follows :

i) Use of the different integro-differential equations - like for example,the Born-Green-Yvon-Bogolubov or the Kirkwood integral equations, or the various forms of the Hypernetted Chain and the Percus-Yevick equations (48,51) - implies the introduction of slightly different approximations, which are not easily interpreted in physical terms. Attempts to do this are mostly based on diagrammatic expansions (50-52). Relative merits of the different equations seem to depend on the fluid density at which they are applied.

ii) Interaction potentials of necessarily somewhat idealised form have to be assumed. It appears in fact, that even for simple liquids like argon, small three-body interaction contributions, do have a small but noticable influence on the molecular structure.(52-54)

iii) Pair distributions determined from diffraction experiment are necessarily somewhat inexact.(55)

It is against this background, that the contribution made by computer experiments must be seen. Beyond providing detailed and accurate information about the structure of realistic model liquids, MD (and MC) calculations have been of great importance for the development of theoretical approaches, by making it possible, to study the effects of various approximative assumptions in isolation, separately,quasi, which are referred to above, and which are most troublesome because of the "overlap" in their effects.(46)

Turning our attention now more specifically to the liquid <u>surface</u>, we find that the surface thermodynamic quantities are expressible in terms of the singlet and pair distribution functions, in a way analogous to the interior phase. Thus, for a plane surface normal to the z-axis, we can express the surface tension, γ , and the surface energy u_s as(17)

$$\gamma = \frac{1}{2}\int \Gamma_2(\underset{\sim}{r}_{12})\,\psi'(r_{12})\,\frac{x_{12}^2}{r_{12}}\,d\underset{\sim}{r}_{12} \quad ; \quad \psi' \equiv \frac{\partial\psi}{\partial r} \qquad \text{—(2.5)}$$

and

$$u_s = \frac{1}{2}\int \Gamma_2(\underset{\sim}{r}_{12})\,\psi(r_{12})\,d\underset{\sim}{r}_{12} \qquad \text{—(2.6)}$$

where the "superficial pair density" Γ_2, is linked to the pair distribution function $n^{(2)}$ by

$$\Gamma_2(\underset{\sim}{r}_{12}) = \int \left[\, n^{(2)}(\underset{\sim}{r}_1, \underset{\sim}{r}_2) - n^{(2)}_{vl} \right] dz_1 \qquad \text{—(2.7)}$$

In these equations, z = 0 has been chosen at the Gibbs equimolecular dividing surface. $n^{(2)}_{v\ell}$ denotes the pair distribution of, depending on the sign of z, either the homogeneous liquid or vapour phase, and the other symbols are used as in equation (2.4). These expressions will have to be considered in more detail in a later section below. The point we are concerned with at the moment is, that calculation of γ and u_s requires the knowledge of pair and singlet distribution functions not only in the two bulk phases, but also in the interfacial zone.

In this region the singlet distribution $n^{(1)}$ becomes a function of z , $n^{(1)} = n^{(1)}(z)$, and defines the density profile through the surface.

The pair distribution function can no longer be described by the isotropic "radial distribution function", $g^{(2)}(r)$, but will depend on the positions of both molecules in a more complicated way. For the plane surface considered above, $n^{(2)}(\underset{\sim}{r}_1, \underset{\sim}{r}_2)$ can be defined* as a function of three variables, z_1 , the z-coordinate of one particle, φ , the angle between $\underset{\sim}{r}_{12} = \underset{\sim}{r}_2 - \underset{\sim}{r}_1$ and the positive z-axis, and the distance $r \equiv r_{12}$.

A slight generalisation of equation (2.2) allows us to introduce a pair distribution function $g^{(2)}$ by writing

$$n^{(2)}(z_1, \varphi, r) = n^{(1)}(z_1) \cdot n^{(1)}(z_2) \cdot g^{(2)}(z_1, \varphi, r) \qquad (2.8)$$

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* Different choices are of course also possible.

Equations (2.5) and (2.6), linking the thermodynamic quantities to the configurational structure, are exact expressions under the assumption of pair-wise interaction.

However, while the pair distribution functions (PDF) of the interior liquid have been calculated with increasing accuracy, it has not been possible to obtain these functions in the surface region*: neither theoretically by statistical mechanics, nor by computer simulation techniques -for reasons already mentioned -, nor, indeed, experimentally.

Computational and other difficulties have also until recently prevented the use of the statistical mechanics apparatus in its usual form, to obtain the density profile. The results, which have recently been calculated via the integral equation approach, do not yet, however, show a satisfactory degree of consistency. They will be considered in detail in Section IO., when the density profile obtained in the present work is discussed.

The apparent inability of statistical mechanics to readily yield information on the surface structure, has encouraged the development of alternative theories of the liquid surface. Foremost among these, are those approaches, which can be characterized as being based on Quasi-thermodynamics(27—32), and which are applicable mainly for states near the critical point. These methods have also yielded density profiles, even for temperatures far below

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*but see (64) and (65) (c.f. our Section 11 below) the critical point, but the applicability of this approach to obtain structural information outside the critical region is contentious.(40,41)

Some versions of the lattice model theories of the liquid state have also been adapted to deal with the surface, and density profiles have been calculated from the hole model (33–39).(37,38)

The general impression must therefore be, that the physics of the liquid surface is by and large characterised, by the lack of reliable information on the microscopic level. This holds in comparison with the interior phase of classical liquids and, to an even greater degree, when the state of knowledge about the <u>liquid</u> surface is contrasted with that about the <u>solid</u> surface.

The difference in the level of development of the molecular theories for the interior dense fluid, and the surface, is perhaps portrayed in summary form, if one observes that, for the interior liquid, some approximative assumptions have to be made, to <u>calculate</u> the microscopic structure, while for the surface, an approximate microscopic structure has to be <u>assumed</u>*, to calculate thermodynamic quantities .

This forms the basis for a number of calculations of γ and u_s , via expressions like equations (2.5) and (2.6), assuming - often more or less ad hoc - approximate forms for singlet and pair distribution in the surface.

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* this excludes the recent calculations discussed in Sec.10

This approach is exemplified by the early calculation of γ and u_s by Kirkwood and Buff (22), who assumed a step-function for the density profile, and approximated $g^{(2)}$ in the surface region by the radial distribution function of the bulk liquid phase. Other methods have improved the approximation by assuming straight-line (57) or exponential types of profiles (63), and by using PDF's,which are obtained from the RDF's of both the liquid and the vapour interior phases by various methods of interpolation.

Results for γ and u_s obtained in this way, usually show quite reasonable agreement with experimental values. Since these thermodynamic quantities are, however, not very sensitive to all details of the molecular structure, this good agreement does not necessarily always imlpy the realism of the underlying structural approximations.

Increasingly, therefore, interest has focussed on the distribution functions themselves, particularily on the density profile. Some statistical mechanical calculations of the singlet distribution function have now been reported, involving approximations about the PDF in the surface. (57 – 62) Some of these results have shown unexpected features, like a non-monotonic change of density between the two phases. The various results do not yet, however, show a satisfactory degree of consistency.

Our theoretical knowledge about the molecular structure of the simple liquid surface, seems in many ways roughly equivalent to that about the liquid interior, obtaining at about the time just before the integral equation approach to the determination of the molecular structure was first developed.

It is to be hoped, that computer simulation techniques -and particular molecular dynamics - will be able to fill a rôle in this field, similar to the one it has become to play for the interior of classical liquids.

The present work, as the first simulation of a three-dimensional liquid surface, is intended as a small step in this direction .

Our investigation of the liquid-gas interface of argon will be concerned only with equilibrium properties, and will comprise determination (at one temperature) of the following :

a) the singlet distribution (density profile) through the surface zone,

b) the pair distribution function in the surface (and also in the interior liquid lamina)

c) a determination of the surface energy, and

d) the surface tension .

PART II

THE METHOD OF INVESTIGATION

SECTION 3

The Periodic Cell

The physical system under investigation is a plane liquid - vapour interface of argon.It was indicated in the previous section already,that the anisotropy inherent in this situation presents the main difficulty for any computer simulation method of investigation.

The surface is visualised as stretching to infinity in the x - and the y - directions,and for these,periodic boundary conditions of the cell can be used in the usual way.To the problem of how to contain the small number of molecules used in the simulation process in the z - direction (normal to the surface), two basic types of solution present themselves :

The first of these entails containing the particles by the introduction of some extraneous force,simulating perhaps a solid wall of material not taking part in the simulation directly.A more sophisticated method of linking the molecules of the surface region to the bulk liquid,is provided by the use of an artifice like the "Thermal Disruption Matrix" used by Croxton and Ferrier in their two-dimensional simulation (66).

The second type of solution to the problem of anisotropy implies the re-establishment of the necessary symmetry in the z - direction.It is this approach,which has been used in the present work.

The periodic cell has been chosen in the form of a rectangular parallelepiped,of equal dimensions in the x - and y -directions,and considerably elongated in the z -direction.The argon molecules are left to aggregate mainly in a region about half-way between the two faces of the cell,which are parallel to the x -y plane.The physical system simulated is thus a liquid film of finite width,stretching to infinity in the x - and y - directions and exhibiting two free surfaces.*

The deviation of the surface structure of the film, from that of the "bulk liquid" surface,can be expected to be small for a large enough width of the lamina.In practice this width is only limited by the computer time available.

The actual dimensions of the cell were decided by the following considerations.

The width of the cell in the x - and y - directions was made as small as possible.In order not to introduce an illegal periodicity,a molecule may be allowed to interact dynamically only <u>either</u> with another particle inside the cell, <u>or</u> with a ghost-copy of the latter,but never with both at the same time.This is achieved by limiting the interaction potential to a range smaller than a maximum distance R, and making the width of the cell equal to at least 2R.The smallest value of R ,which would be useful for our purpose,was inferred from the known shape of the equilibrium pair distribution for the

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* Since the z - boundaries of the cell are also taken as periodic,the physical system simulated is perhaps more accurately described as an infinite number of parallel identical laminae of this nature.

interior of liquid argon (for temperatures of between 85^0 K and I00°K).

R was taken equal to I0 Å and the width of the periodic cell was chosen as 20 Å in the x - and y - direction.

Since it is our aim to investigate the structure of the interfacial region between bulk liquid argon and its vapour phase,we require the thickness of the simulated liquid film to exceed a certain minimum value.The structure of the two surface regions one obtains for such a film should not be appreciately different from that of a bulk liquid surface.It is estimated that the effect,which the presence of the one surface has on the structure of the other surface,would be small,if both regions are separated by 20 Å to 25 Å of liquid having "bulk" structure.

For cell dimensions of 20 Å in the x - and y-directions,these conditions could be met by chosing the number of argon atoms used inside the cell to be not less than 300.

300 particles would form a liquid film of thickness 40 Å to 50 Å, and most calculations reported in this work were done for this number of molecules in a periodic cell of dimensions of 20Å x 20Å x 80Å (Fig.1)

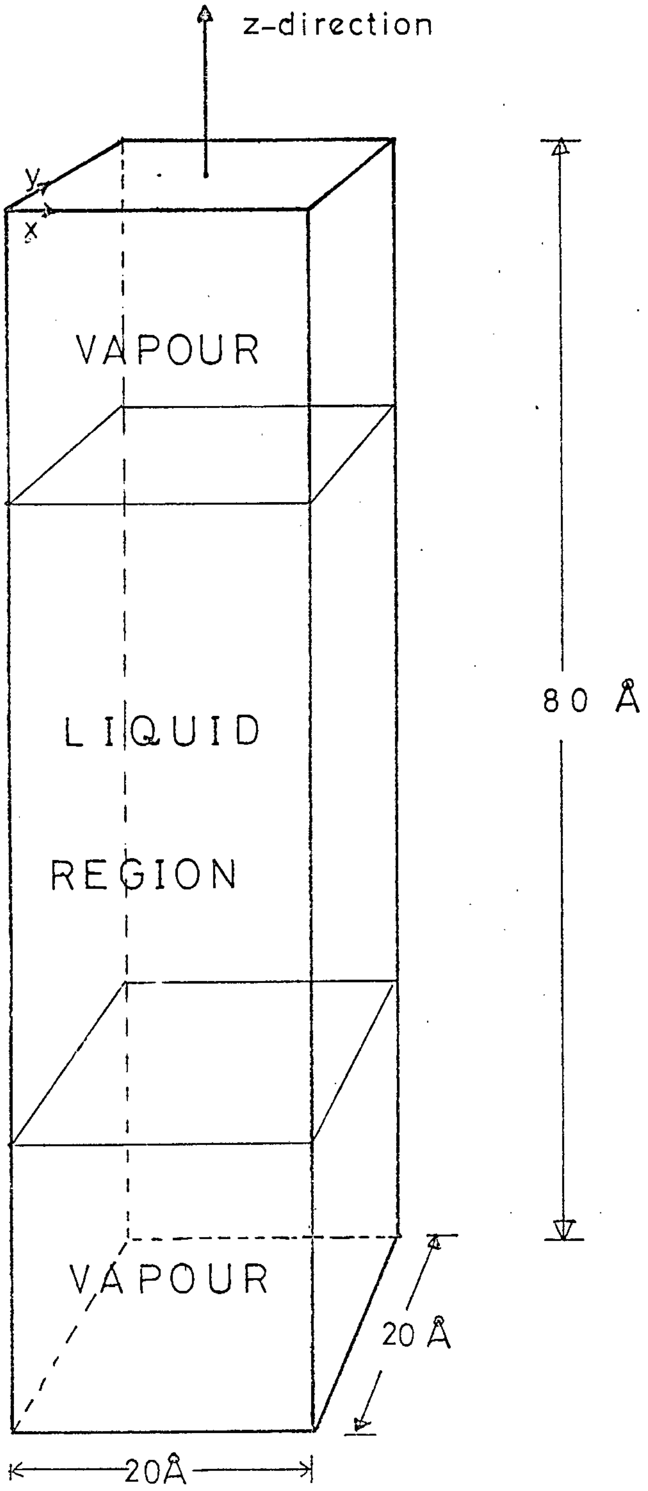

FIG I :The cell.Periodic boundary conditions were assumed in all three dimensions.

SECTION 4

The Interaction Potential

4.I On the choice of potential

There are a number of reasons, why it was decided to use the more realistic Lennard-Jones interaction potential,rather than a square-well or hard-sphere potential,which would have shortened the computation time.

This was done to avoid obtaining a molecular structure in the surface, which showed deviations from the rather well known Lennard-Jones liquid structure due to a superposition of three effects :

i) the existence of the phase boundary

ii) the rather idealized nature of the interaction law, and

iii) the finite width of the lamina

Although point iii) would presumably be compensated for by our ability to use a lamina of greater width,it was felt to be desirable, to obtain values for the thermodynamic surface properties,surface tension and surface energy,at the same time as investigating the microscopic structure.Comparison of these thermodynamic quantities to experimental results,does give some indication of how successful the simulation of the surface is, but pre-supposes the use of a fairly realistic interaction law.

It was decided to use a two-body interaction law between molecules, in spite of the known fact, that the small three-body potential terms do seem to have a noticable effect on the structure of liquid argon(52-54) Methods which might allow the inclusion of three-body terms without increasing computer time excessively would, however, be difficult to apply in the presence of such a strong density gradient as found in the surface(54)

At a future time, when the equilibrium structure of the surface zone might be known with better accuracy, a calculation including three-body interactions might, however, prove to be interesting, exactly because the effect of these terms can be expected to be of greater importance in an anisotropic situation.

4.2 The Modified Lennard-Jones Potential used

The interaction potential $\psi(r)$ was chosen as essentially of the Lennard-Jones form, with values of σ and ε appropriate for argon (σ=3.45 Å, ε = 1.601 x 10^{-14} erg (43)) It was modified in the following way :

I) for distances r from 0 → 8 Å

$$\psi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad \text{(Lennard-Jones 12-6)} \quad -(4.1)$$

2) from 8 Å → I0 Å , a linear form was chosen between the Lennard-Jones value at 8 Å and the value zero at r = I0 Å .

i.e. $$\psi(r) = -\frac{1}{2}\psi(8)\cdot(r-10) \qquad \text{—(4.2)}$$

3) $\psi(r) = 0$ for $r > 10$ Å . —(4.3)

An abrupt cut-off of ψ(r) at r = I0 Å would be a source of fluctuations in the total energy of the system, which, although basically random in nature in an equilibrium situation, cannot be reduced by decreasing the size of the time steps in the integration process.The potential used assumes a somewhat greater attractive force between eight and ten angstrom, but this only serves to somewhat counteract the effect of assuming <u>no</u> attraction beyond ten Angström.

SECTION 5

The Numerical Integration Process

5.I On the Algorithm used

In the present work, the numerical integration of the equations of motions was performed using a straightforward Taylor expansion for the positions and momenta.

For the i th particle, we can expand with respect to time, using an obvious notation,

$$\underset{\sim}{r}_i(t+\Delta t) = \sum_{\nu=0}^{\infty} \frac{1}{\nu!} \frac{d^\nu \underset{\sim}{r}_i}{dt^\nu} \cdot (\Delta t)^\nu \qquad \text{— (5.1)}$$

$$\underset{\sim}{p}_i(t+\Delta t) = \sum_{\nu=0}^{\infty} \frac{1}{\nu!} \frac{d^\nu \underset{\sim}{p}_i}{dt^\nu} \cdot (\Delta t)^\nu \qquad \text{— (5.2)}$$

The classical equations of motion are then used to express the various terms (up to a certain order in Δt) in terms of the forces acting on each molecule .

For deciding on the number of terms to be included in the Taylor expansion, and on the size of the time step Δt, the following two points had to be considered :

I) The integration has to be close enough. As criterion, the stability of the total energy of the system was used.

2) Using available computer time, it had to be possible to simulate the system long enough to obtain statistically meaningful averages for equilibrium properties of the system.

Enhanced energy stability is achieved by :

a) including higher terms in the Taylor expansion, and

b) using a smaller value for Δt.

In either way, the necessary computer time is increased, and therefore a certain balance has to be struck. Since it seems difficult -if not impossible - to calculate the optimum choice theoretically, a number of preliminary computer experiments were performed.

5.2 Preliminary Computer Experiments

Information on the above question could have been obtained in the most direct way, by simulating the full 300 particle system for various combinations. It was felt, however, that preliminary MD calculations of this nature would require too much time.

It was therefore decided, to use two smaller systems for this purpose.

The effects due to the finite time step and the truncation of the Taylor expansion, must be expected to be greatest at small interparticle distances, where the potential is steepest.

MD simulation experiments were therefore performed on collisions between two particles, interacting via our modified Lennard-Jones 12-6 potential, and having kinetic energies somewhat above those in the liquid.

The two particles were given a certain total energy, starting off at a large distance, and the collision process was then simulated for a particular choice of Δt and the number of terms considered in equ.(5.3,4). After each step the total energy was determined, and the deviation of this quantity from its initial value was plotted as a function of time.

This was repeated for various choices of Δt and orders (in (5.3)) and information was thus obtained on the maximum deviation of the total energy from its ideal value, and on the "error" remaining after the particles had separated again.

These calculations were done for various "collision" parameters.

Although these calculations provided information about the errors implied by the different choices, they were found not very suitable to determine the increase in computer time caused by the inclusion of successively higher terms in the expansion.

This can be inferred more easily from the simulation of a more complicated system.

The second type of preliminary simulation experiment used a three-dimensional system of 20 particles, interacting via a Lennard-Jones I2-6 potential.

Besides yielding information on the questions mentioned above, this system was used to investigate a few other problems, and was found to be of some interest for its own sake.

Simulations of the 20 - molecule system, were thus carried out at various "temperatures", assuming different interaction laws, and using a number of different external potentials to enclose the system in a " box". Densities in three mutually perpendicular directions were monitored and the molecules enclosed in the "box" were observed to aggregate, to form a 20-molecule "particle". This "particle"was then observed to move through the box as a whole, suffering distortions in shape on impact with the walls, ejecting single molecules to form a "vapour phase" and so on.

Besides being of some entertainment value, these

20 - particle simulations provided much useful information used in the main calculation (by example, about the design of averaging routines for pair distributions etc.).

These investigations were intended only as preliminary experiments for the main surface simulation, and the results obtained have not been published.

5.3 Some Remarks about Computing Procedures

From these preliminary calculations, it was decided to take as time step Δt = 0.0I ps (i.e. = 10^{-14} sec), and to use terms in the expansion up to and including $(\Delta t)^2$ only. Similar values for Δt have been used in a number of MD calculations for the liquid state(5-7,46)

Justification for our value for Δt is more directly derived from total energy stability considerations, but we can also compare Δt to the Einstein frequency of the liquid, which we can define by

$$\omega_E = \left(\frac{\langle a^2 \rangle}{\langle v^2 \rangle}\right)^{\frac{1}{2}} \qquad -(5.5)$$

a and v are acceleration and velocity of a particle and the symbol $\langle\rangle$ indicates averages (7).

ω_E for argon at our density is reported to be about $\omega_E = 0.7 \times 10^{13}$ (sec^{-1})(7). The value for $\Delta t \cdot \omega_E$ which we obtain is thus equal to 0.07 ,which is fairly small. It is about a third of the value reported possible in a MD calculation using Beeman's algorithm (7). This shows, unless we have made Δt unnecessarily small, the superiority of Beeman's algorithm.

Total energy stability for our system of 300 particles(but interacting of course with "ghosts") was better than 0.4 % per 1000 steps,and this was considered good enough for our purpose.

The calculating routines were of course arranged, so as to shorten the time necessary per step,as far as seemed feasible.

The program was written entirely in FORTRAN V and the computer used was the UNIVAC 1106 system of the University of Cape Town.

It was found that the computer time necessary to advance the simulation process by 100 steps (i.e. for 1 ps), was about 25 minutes. This time includes the execution of the averaging routines, for the various quantities to be determined.

Averages for surface properties had to be taken over periods of 50 ps or more, to obtain statistically significant results. In order to continue the simulation for this long time, the program was arranged in such a way, that short runs of duration of up to about 25 minutes were made. All relevant information, like positions and momenta of all particles, were stored on magnetic disc at the end of each run, from where it would be read by the next.

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Averaging procedures were initiated automatically at certain intervals, and the whole simulation process was continued in this way over a period of some month , for about I0000 time steps.

SECTION 6

The Attainment of an Equilibrium State

6.I Some General Remarks

The thin-lamina system simulated here is un-physical in the sense,that it is not known, whether such a system would be stable in nature.In fact, it does not seem very likely.

The use of such a system to gain information on the equilibrium free surface of bulk liquid, therefore appears problematical on two levels :

Firstly, it was not known, whether a liquid film of this small width would be stable even on a very short time scale.Thus, some care had to be taken to ascertain that such a stable state had indeed been reached, and that averages for surface properties were not obtained while the lamina was still (noticably) evolving towards a different state (e.g. "solidifying", evaporating, or breaking up).

Secondly, if and when a stable state can be reached, it must be assumed, that the molecular structure of the lamina may differ somewhat from the system, at which the investigation is aimed.We will consider this point in detail in Section 8.

In the present section, after considering the initial starting-off procedure, we will enumerate and briefly discuss the various quantities, which had to be monitored to observe the attainment of a stable state, and to investigate the nature of the molecular structure in the interior of the lamina.

6.2 The Starting-off Procedure

The system was started off with the argon atoms positioned in a simple cubic array, forming a lamina of width equal to about 40 Å in the centre of the periodic cell.The array was chosen so as to give a density approximately equal to the density of liquid argon.In contrast to M.D. and M.C. calculations using a cell with periodic boundary conditions to simulate bulk material, the choice of the density is not critical here, because the liquid film can contract or relax to attain the correct density appropiate for the temperature and pressure.

This was indeed observed.All atoms were initially given small velocities in random directions, and then let develop according to the classical equations of motion. The simulation process was repeatedly interrupted and the momenta adjusted, until the average kinetic energy levelled off at a certain value.

The first quantity, thus, which we can consider in some more detail, is the kinetic temperature.

6.3 The Kinetic Temperature

A quantity we will call "kinetic temperature" can be defined by the expression

$$T = \frac{2}{3Nk} \cdot KE \qquad — (6.1)$$

where k is Boltzmann's constant and KE indicates the kinetic energy of the system of N (= 300) particles. The temperature we will ascribe to the equilibrium state of the system, is then taken as the time average of T .

Initially, when the system was started off, each particle was given a very small velocity, almost all of the total energy being thus potential energy.As the system developed, the kinetic energy (and thus T) was several times artificially adjusted, this "intervention" taking the form of multiplying all momenta by a constant factor.

When the ratio of potential to kinetic energy seemed to stabilize, and T began to fluctuate about a temperature value appropriate for the liquid state, the system was left to continue freely.The start of the actual simulation experiment is thus really marked by the last "artificial" adjustment of the kinetic energy.

It was decided at that stage, not to try to force the system towards a state corresponding to an exact predetermined temperature by continued outside adjustment, but to continue the experiment at the temperature

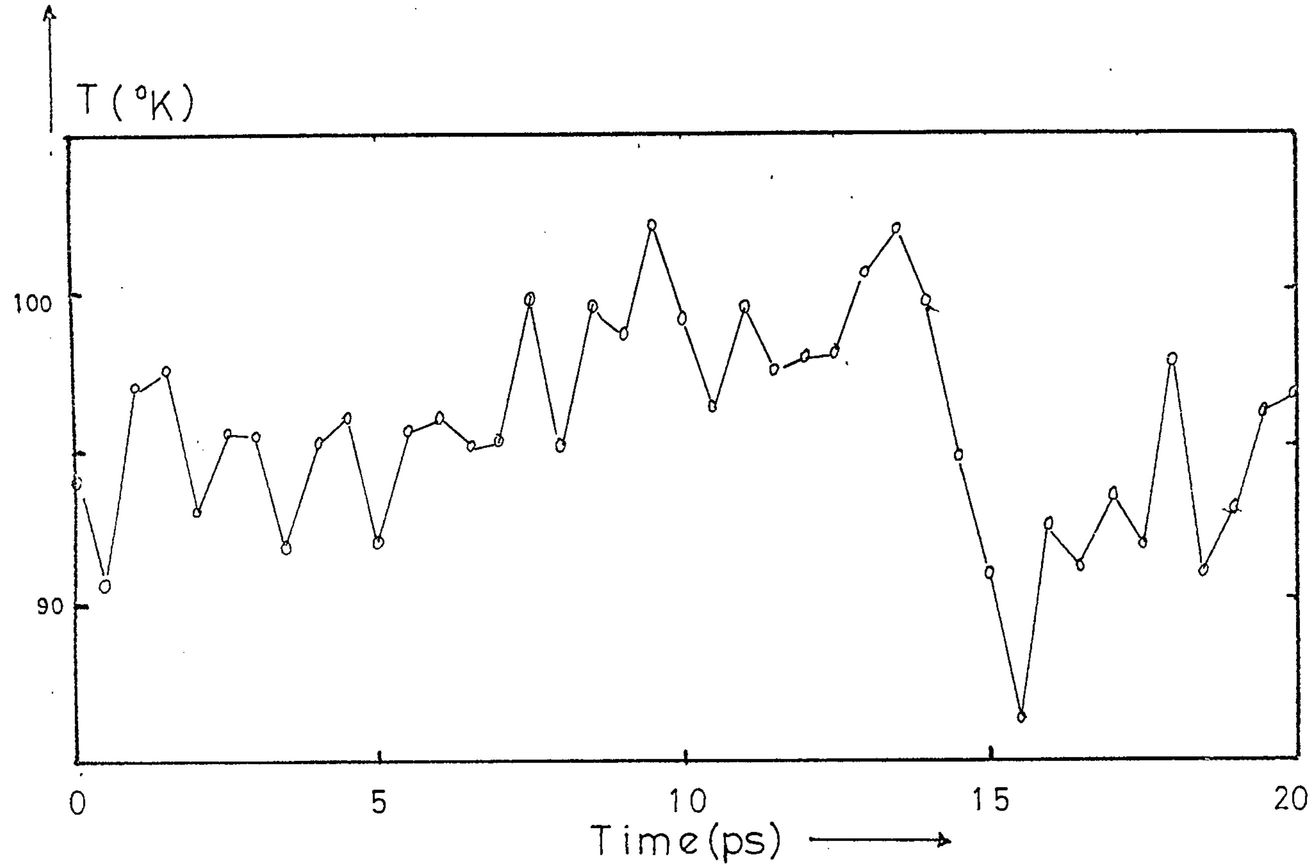


FIGURE 2

Fluctuations in the kinetic temperature, T , over a period of 20 picoseconds .

for which it seemed to have stabilized at that stage.

T was measured at intervals of 0.5 ps (every 50 steps) throughout the simulation experiment, the cumulative average of T indicating a temperature of about 97.1°K (± 0.15°K).

The variation of T over a period of 20 ps is shown in Fig. 2 .

6.4 The Momentum Distribution

The small momenta given to all molecules initially, were all of equal magnitude (though having different directions).The approach of the predicted Maxwell distribution, from this initial state was fairly fast; somewhat faster then the attainment of a definite configurational structure.In Fig. 3 the momentum distribution for the 300 molecules, obtained at irregular intervals over a period of only 30 ps , is plotted, showing the well-known shape. The Maxwell distribution is given by

$$f(p) \propto \exp\left\{-\frac{p^2}{2mkT}\right\} \qquad -(6.2)$$

Comparison of the experimental distribution with this was therefore more easily effected when f plotted against $\exp\{-p^2\}$.

To obtain the momentum distribution in a short time, rather large intervals (in momentum) were used, and this finite resolution unfortunately causes a systematic

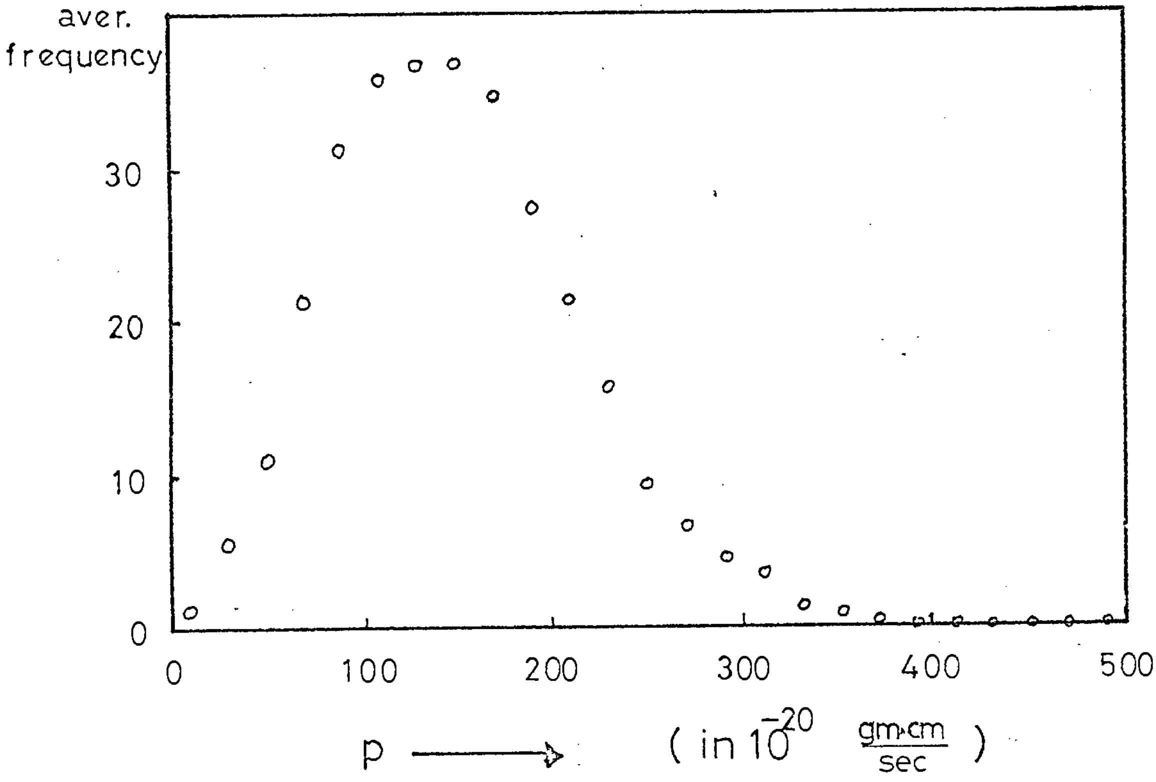


FIG 3 : The momentum distribution for the system of 300 particles. This distribution represents the average over only 30 picoseconds.

deviations from the ideal form. Molecules in the vapour regions can also be expected to require much longer times before conforming to the theoretical distribution.

Apart from these points, one has to conclude, however, that the simulated system did attain a state described by the Maxwell form.

6.5 The Interior Density and the Density Profile

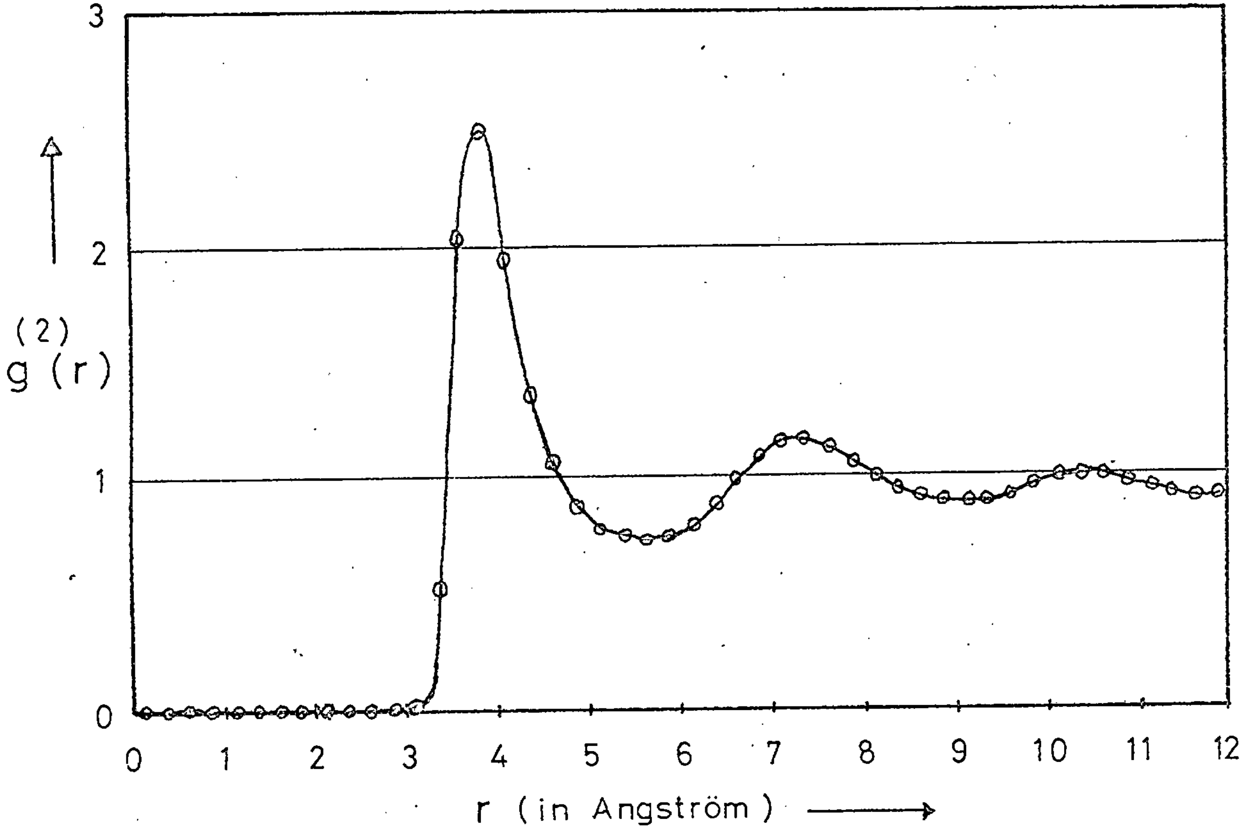
The number density throughout the cell, was monitored in three mutually perpendicular planes during the experiment.

In the central (interior) region of the lamina, $n^{(1)}$ was observed to change from the periodic form associated with the initial array, to a constant value of 1.675x10^{-2} per Å^{3}.

To obtain the density profile through the surface was of course one of the main aims of this whole investigation.The observed change from the initial abrupt cut-off to a certain final shape was, however, also found to provide one of the most easily recognized indication of the system's approach towards a stable state .

6.6 The Pair Distribution of the Interior Region

Since it was our aim to investigate the structure of the surface region between bulk liquid and its vapour, it was important to establish, that the interior of the liquid lamina showed an equilibrium structure similar



<u>FIG 4</u>: The radial distribution function found for the interior of the liquid lamina. The mean density in this region was I.I2 gm/cm^3 .

to that of bulk liquid argon. For this reason, the radial distribution function $g^{(2)}(r)$ was obtained for this central region. The resolution used was $\frac{1}{4}$ A and the curve is shown in Fig. 4.

It seems in good agreement with previously reported radial distribution functions for liquid argon (8,67)

The function $g^{(2)}(r)$ obtained here, was also used as "reference" function for our investigation of the pair distribution in the surface.

As judged by the above points, the system reached an equilibrium state approximately 10 ps after it was started off. Averaging for equilibrium properties was begun after a further 10 ps of simulation, and it was observed, that these quantities seemed not to change appreciably during the next 90 ps .

It is to be noted, however, that all quantities referring specifically to the low density regions(gas phase) did not show this fast progress towards equilibrium values, and in fact tended to still show appreciable fluctuations after 100 ps. This is however not surprising, since one should expect the relevant relaxation times to be inversely proportional to the densities.

Secondly, it is realized , that in macroscopic terms, even 100 ps still represent a rather short time period. The fact that the "interior" radial distribution did, however, approach the generally accepted equilibrium form, does lend weight to the view, that the surface structure of the "stable" state reached, can be used to obtain information on the bulk liquid - vapour surface in equilibrium.

It is of course not possible to base the interpretation of our results merely on a qualitative statement like the above. The relation between our simulated system and the macroscopic free surface,at which this investigation is aimed, will in fact have to be discussed in some detail and in quantitative terms, before the relevance of our results is established.This will be done in Section 8 .

SECTION 7

On the Determination of the Surface Properties

In this section, we will discuss the methods used, and some of the underlying assumptions, for the determination of the surface quantities, which were investigated.

Some of the details given here, are only included for the reason, that no computer simulation of a liquid surface has been reported up to now.* No "proven methods" exist therefore for the determination of the surface properties, and some points (difficulties,mostly), which arise in our methods, are mentioned only, because they are peculiar to the surface situation, and are presumably met here for the first time, and not because they are necessarily of great inherent interest .

7.I The Determination of the Specific Surface Energy

Our aim was to obtain the specific surface energy for a macroscopic plane surface (of argon) from our MD simulation experiment.

Before we can dicuss our method used to find it, we have to consider a definition of this quantity.

Following the approach of Gibbs (9), we can define

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* This refers to a three-dimensional liquid.For a two-dimensional model of a liquid, Croxton and Ferrier have reported a MD simulation of the surface (66) .

the surface energy U_s by writing

$$U = U_l + U_v + U_s \qquad -(7.1)$$

Here U is the actual internal energy of the whole system, including the liquid phase, the interfacial region and the vapour phase; U_l is the internal energy of the liquid phase assumed homogeneous up to a Gibbs dividing surface, U_v is the corresponding quantity for a vapour phase assumed homogeneous up to the same dividing surface.

The quantity of interst is the "specific surface energy ", that is U_s per unit area, for which we will use the lower case symbol u_s .

The internal energy can be expressed as the sum of two terms, one corresponding to kinetic energy, the other to potential energy . Thus we can write for the internal energy per unit volume in the interior of homogeneous bulk liquid , $\hat{u}_l$

$$\hat{u}_l = \frac{3}{2} kT \cdot n_l + \hat{w}_l \, n_l \qquad -(7.2)$$

where n_l is the constant number density in the liquid phase and $\hat{w}_l$ indicates the average potential energy per molecule in the liquid.

Similar expressions can be written for the vapour phase and the surface region, and it is easily shewn, that u_s can be calculated from the potential energy contribution alone, if the equimolecular dividing surface is chosen as the Gibbs dividing surface.

The expression for u_5 becomes then

$$u = w - w_\ell - w_v \qquad -(7.3)$$

The location of the equimolecular dividing surface is given by

$$z_E = \frac{1}{n_\ell^{(1)} - n_v^{(1)}} \cdot \left[\int n^{(1)}(z)\, dz + z_\ell n_\ell^{(1)} - z_v n_v^{(1)} \right] \qquad -\cdot(7.4)$$

here z_ℓ and z_v are assumed to be situated far inside the homogeneous liquid and vapour phase respectively.

This dividing surface was used in the present case. The position of the equimolecular surface was obtained from the density profile by a graphical method, and is indicated in Fig.9

The average potential energies w, w_ℓ and w_v were obtained from the simulated system. For this purpose, the ordinary Lennard-Jones interaction potential was used rather than the modified form used in the integration process . w_ℓ was found by determining the average potential energy of molecules in the interior of the lamina, and w_v from those in the vapour region, far from the surface. For the determination of w, the whole simulated system was used, including the surface regions, the result thus being, in a sense, an average over both surfaces.

The following points had to be considered, however : The range for which individual interactions between molecules could be considered, was again limited to IO Å. To account for the effect of molecules at separations greater than IO Å , $g^{(2)}(\underset{\sim}{r}_1, \underset{\sim}{r}_2)$ was assumed equal to unity beyond that distance, and correction terms were calculated.

This was a simple matter for the determination of w_ℓ and w_ϑ, but was found to be somewhat involved for w , since the density profile through the surface itself had to be used for this purpose.

Further correction terms were added to account for the interactions between those parts of a macroscopic surface system, which would be lying outside our periodic cell (i.e. in the z-direction).

The result was thus intended to represent the specific surface energy for a plane surface of macroscopic dimensions, rather than a lamina of finite width.

7.2 The Determination of the Surface Tension

The approach used in the calculation of the surface tension,was basically similar to that for u_s .

We can use a mechanical definition for the surface tension of a plane surface

$$\gamma = \int_{-\infty}^{+\infty} \left(P - P_T(z) \right) dz \qquad \text{— } (7.5)$$

P_T is the tangential component of the pressure tensor, which for the plane surface is a function of z only(i.e. $\underline{p}_{xx}$

or p_{yy}, p_{xx} was used). p_{xx} is the sum of two contributions , the kinetic part, due to the momentum transport of the moving particles across the unit area, and a " static" contribution, due to the forces between molecules.

By referring γ to the equimolecular dividing surface (at z_E) we again effect the cancellation of all kinetic contributions, so that equation (7.5) becomes

$$\gamma = \int_{-\infty}^{+\infty} \left(P_{l v} - P_T(z) \right) dz \qquad \text{--(7.6)}$$

where the symbols refer now to the "static" part alone. $P_{l v}$ takes the values appropriate to the homogeneous liquid or vapour phase, depending on whether z is smaller or greater than z_E . The integrand thus becomes zero both inside the liquid and inside the vapour.

$P_{l v}$ was determined by obtaining averages for the stress in the interior of the lamina, and in the vapour respectively (the latter quantity was found to be almost negligible), and the tangential stress component was found by averaging the x-components of interparticle forces, acting across a mathematical surface normal to the x-direction, for the whole system.

Interactions between molecules were considered explicitely again only for distances of up to 10 Å .
To account for particles at greater distances, $g^{(2)}$ was again taken equal to unity, and correction terms were

calculated. The calculations for these terms was fairly complicated, and some approximations had to be made, but their relative contribution to the value for was less, than was the case for u_s (only about 5 %), because the interparticle force falls off with distance even faster than the potential.

7.3 The Investigation of the Density Profile

One particular difficulty inherent in a computer simulation of a liquid surface, stems from the fact, that one has to simulate regions of both, high and low densities, at the same time. The large number of particles necessary, and the energy stability conditions applying to the high density region, require a large amount of computer time - the progress in the simulation is slow.

The time necessary to obtain statistically meaningful result for quantities connected with the surface or the vapour region of the system, is,on the other hand rather long, much longer than would be the case for a ordinary dense system, since these times are approximately inversely proportional to the density.

Thus one finds, that a simulation of the surface requires a particularily large amount of computer time before results can be obtained.

In the face of this difficulty therefore, a compromise had to be made about the resolution, with which distribution functions in the surface could be determined in this MD experiment.

It was also not known at the beginning of the simulation experiment, for how long averages would have to be taken. Our approach has mostly been, to use a rather optimistic resolution in the measurement process, and to use these measured values to obtain the function with a much poorer resolution, as long as this was necessary.

As the simulation process was continued, distribution functions could then be determined with progressively greater accuracy, and more detailed insight in the molecular surface structure could be gained. The simulation was not continued long enough, however, to be able to always accept as statistically significant, information on the level of the best (measured) resolution - this would in some cases probably require quite unrealistically long simulation times (for the present MD program).

We will now turn particularily to the determination of the density profile through the surface.

The quantity we want to investigate is the "singlet distribution function"in this region.

In a notation suitable for the Canonical Ensemble (N is the number of particles), we can define this configurational distribution function of the lowest order, $n^{(1)}(\underset{\sim}{r})$, as the probability density of finding a molecule at position $\underset{\sim}{r}$, with the normalization

$$N = \int n^{(1)}(\underset{\sim}{r})\, d\underset{\sim}{r} \qquad - (7.7)$$

For the interior of a fluid phase, $n^{(1)}$ becomes the ordinary number density, which is usually a constant in an equilibrium situation, while for our plane surface $n^{(1)}$ is a function of z only.

The computer routine used for obtaining information on $n^{(1)}(z)$, therefore divided the periodic cell into I60 parallel "strips", or regions, normal to the z-direction, and each of width equal to $\frac{1}{2}$ Å . Averages were taken at intervals of I ps for about 75 ps, and the density profile could thus be obtained with a resolution of (theoretically) $\frac{1}{2}$ Å .

Our simulated system contained of course <u>two</u> plane surfaces, and the density profile was thus obtained for both at the same time. It was however decided, not to derive some average profile from these two, but to observe both surfaces separately. The reason for this is, that is was thought to be not too easy, to form such an average in a satisfactory way. In particular, by combining the two functions, with one slightly shifted with respect to the other, due perhaps to a slight asymmetry in the lamina, all kinds of spurious and misleading features could have been produced in the "average" profile.

7.4 The Investigation of the Pair Distribution Function

The pair distribution function was investigated for both, the surface zone, and the interior of the lamina. We have defined this function already in Section 2 and will now give some information on the methods used for this investigation.

In the interior of the liquid lamina, the pair distribution function was assumed to be a function of the interparticle distance only (and this was verified), described thus by the radial distribution function(RDF). This RDF was thus determined with respect to "reference molecules ", which had to be found within a distance of 4 Å from a "central z-plane" through the centre of the lamina. $g^{(2)}(r)$ was obtained for values of r from 0 Å to 12 Å, with a resolution of $\frac{1}{4}$ Å.

To choose suitable averaging procedures for investigating the pair distribution function (PDF) in the surface zone itself, was slightly more difficult.

In the general case, we can write the pair distribution $n^{(2)}$ as

$$n^{(2)}(\underset{\sim}{r}_1,\underset{\sim}{r}_2) = n^{(1)}(\underset{\sim}{r}_1)\cdot n^{(1)}(\underset{\sim}{r}_2)\cdot g^{(2)}(\underset{\sim}{r}_1,\underset{\sim}{r}_2) \qquad -\ (7.8)$$

thus defining the PDF $g^{(2)}(\underset{\sim}{r}_1,\underset{\sim}{r}_2)$ as a generalisation of the radial distribution function.

It follows from equation (7.8) and the definition of n that

$$g^{(2)}(\underset{\sim}{r}_2, \underset{\sim}{r}_1) = g^{(2)}(\underset{\sim}{r}_1, \underset{\sim}{r}_2) \qquad -(7.9)$$

In the case of a plane liquid surface, where the density gradient exists only in the z-direction, $g^{(2)}(\underset{\sim}{r}_1, \underset{\sim}{r}_2)$ will be a function of only three variables. For this investigation, the most suitable choice of variables seemed to be (z_1, φ, r). z_1 is the z-coordinate of one particle, φ is the angle between the vector $\underset{\sim}{r}_{12} = \underset{\sim}{r}_2 - \underset{\sim}{r}_1$ and the positive z-direction, and $r = |\underset{\sim}{r}_2 - \underset{\sim}{r}_1|$.

Two factors served to limit the accuracy, with which we could determine $g^{(2)}$ in the surface :

The first, on which we have already remarked, is the difficulty encountered of obtaining statistically significant results for functions reaching into the regions of lower density.

The second lies in the fact, that we are concerned here with a function of three variables. The resolution with which such function can be obtained for all three variables, is severely limited by the amount of data which can be dealt with - even by computer. This is especially so in this case, where these data do not only have to be stored, but also have to all be updated every 100 or 50 simulation steps.

With this in mind, information on $g^{(2)}$ in the surface region was obtained as follows :

Values of z_1 were restricted by considering as "reference molecules" only particles found within one of 20 narrow "strips" (each of width I Å in the z-direction), which were arranged at regular spacings, with IO in each surface zone.

The dependence of $g^{(2)}$ on φ was investigated by recognizing only 5 different directions, namely one in the direction of the density gradient, another at right angles to this (parallel to the surface), and three more intermediate directions. Fig.5 indicates the arrangement, and shows also, that the r-dependence was established in both the forward direction(i.e. towards the gas phase) as well as the "backward" direction. In each case the radial variation of $g^{(2)}$ was investigated for values of r from zero to I2 Å, with a resolution of $\frac{1}{4}$ Å.

The total information obtained about $g^{(2)}$ was then contained in an array of 20 x 5 x 96 .

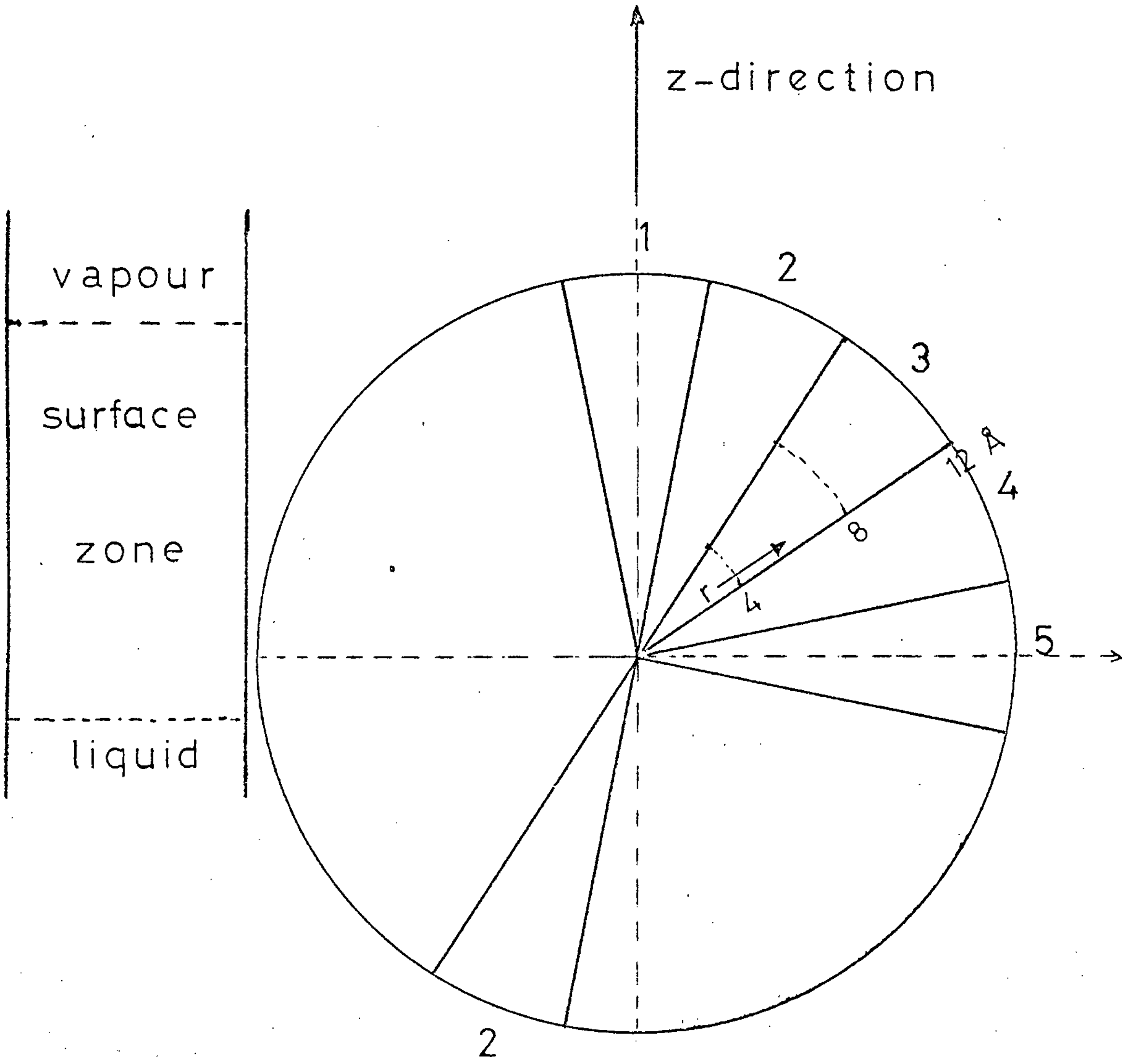

FIG 5: Diagram showing the arrangement for investigating the ϕ-dependence of $g^{(2)}(z_1,\phi,r)$ .Only five distinct directions, numbered I to 5 ,were recognized.For the sake of clarity, the"backward" direction has only been indicated for No.2

PART III

RESULTS

SECTION 8 : The Effect of the finite Width of the Lamina

SECTION 9 : Surface Tension and Surface Energy

SECTION I0 : The Density Profile

SECTION II : The Pair Distribution Function in the Surface

Some General Remarks

SECTION 8

The Effect of the finite Width of the Lamina

By simulating a film of finite width, it has been possible to obviate the problem posed by the anisotropy associated with a plane surface. It has been further concluded from the facts summarized in Section 6. , that such a system can be simulated for long enough times to investigate its molecular structure.

The fact remains however, that our system is different from the one about which information is really sought - the interface between bulk phases .

Before discussing the results obtained, we must therefore consider, in how far our results are of relevance for the macroscopic interface.

The kinetic temperature, at which the simulation was carried out, was equal to about 97.I°K . It was found at the same time, that the mean number density at the centre of the film was I.675 x $I0^{-2}$ atoms/$Å^3$, which corresponds to a density of I.I2 gm/cm^3 .

We note, that these values are not in agreement for bulk liquid argon in equilibrium with its vapour. For this case, the density found for the interior of the liquid film would correspond to a temperature of about I24° K (43)

There exists, therefore, a significant difference between the equilibrium state reached by the simulated lamina, and that of a free surface of a bulk sample. This difference, which is due to the finite width of the lamina, must also imply a difference in the molecular configurational structure, both for the central "bulk" region, and for the surface zone, and cannot simply be neglected. Fortunately, this is also not necessary.

The interpretation of our results is based on the generally known fact, that the configurational structure of a simple classical liquid depends on temperature almost exclusively via the density.(46)

The experimental evidence for the interior liquid phase shows, that the pair distribution function $g^{(2)}$ would be essentially the same for two states of the same mean density, but having different temperatures (and pressures). (67)

Evidence of this phenomenon, more specifically applying to the surface region, is provided by the temperature independence of the parachor.

Following Sugden(68), we can define the parachor P by

$$P = \frac{\gamma^{\frac{1}{4}}}{n_l - n_v} \qquad (8.1)$$

γ is the surface tension, n_l and n_v are the number densities of the liquid and vapour phases.

It has been found, that the parachor - for any given substance - remains very nearly independent of temperature over a wide temperature range (43). In fact, it has been shown by Lennard-Jones and Corner (33 , 36), that P can be linked directly to the parameters ε and σ of the Lennard-Jones I2-6 potential by

$$P = (7\cdot 1 \times 10^{23}) \cdot \varepsilon^{\frac{1}{4}} \cdot \sigma^{\frac{5}{2}} \qquad -(8.2)$$

an expression, which was found to be exact to within 3.6 % for various liquids.

Thus, from equ.(8·1), or by re-writing that expression as

$$\gamma = P^4 (n_\ell - n_v)^4 \qquad -(8.3)$$

which is a particular form of McLeod's Equation(69), we can see, that the surface tension depends only on the densities of the two phases.

In view of the fairly complicated dependence of γ on the distribution functions, and the analogy with the bulk liquid phase, it seems reasonable — though not logically compelling — to infer from these indications, that the configurational structure in the surface should also depend on the densities only. Even if not strictly true, this appears to be at least a good approximation. Some further evidence for our interpretation is supplied by this computer simulation itself and will be discussed in the next section.

The underlying cause of this, for our purpose fortunate, property of classical simple liquids, must be sought in the steepness of the repulsive part of the interaction potential.(46)

From these arguments we conclude, that we should accept as basis for the interpretation of our results, the following view :

we are simulating a surface of liquid argon, which is defined by the measured densities of the two phases. This surface is most closely analogous to a macroscopic free surface at a temperature of I24°K, and the results obtained from this MD calculation are therefore interpreted as yielding information on a free surface at this temperature.

SECTION 9

Surface Tension and Surface Energy

The relevance of the results obtained in the present work, and the suitability of our basic method as a MD calculation in the liquid surface, does obviously depend to a great extent on what has been said in the previous section. We therefore may take the view, that any importance, which may be attached to the values for γ and u_s found here, does not only lie in their being determinations of thermodynamic surface properties by a MD method, but also in the role they can play in underpinning the above argument .

Before persuing this point further, we will now look at the actual values obtained. Both, surface tension and surface energy, will be considered together.

The values found were

$$\left.\begin{aligned} \gamma &= 4.2 \pm 5\% \quad (\text{dynes/cm}) \\ u_s &= 28.17 \pm 4\% \quad (\text{erg/cm}^2) \end{aligned}\right\} \qquad \text{—}(9.1)$$

Contributions to the estimated uncertainties indicated, arose mainly from the following causes :

i) Remaining statistical fluctuations contribute considerably to the uncertainties, since averages were taken over a period of only 40 ps. This effect is of greater relative importance for the surface tension.

ii) The uncertainty in the location of the equimolecular dividing surface has some effect. Both quantities were calculated with reference to the Gibbs equimolecular dividing surface, so that kinetic contributions to γ and to u_s did not have to be considered.

The location of the equimolecular dividing surface was determined from the density profile by a graphical method, probably to within ± 0.3 A . For a more accurate determination, the profile itself would have had to be available with a better resolution.

iii) Various approximations, used in the calculation of γ and u_s have been mentioned already in Section 7. These must be considered additional sources of error.

iv) We must note, finally, that our values obviously depend on the parameters of the assumed Lennard-Jones potential.

In order to facilitate comparison with experimental and theoretical values reported in the literature, we will "reduce" our results from a temperature of I24°K , for which they are taken to apply, to equivalent values at 90°K.

A well-known equation for the temperature dependence of the surface tension is the semi-empirical Katayama-Guggenheim formula (44,45) :

$$\gamma = \gamma_0 \left[1 - \frac{T}{T_c} \right]^{11/9} \qquad \text{—(9,2)}$$

where T_c is the critical temperature and γ_0 is a constant. For argon, these values are $T = 150.7\,^{\circ}K$ and $\gamma_0 = 36.31$ dynes/cm.

This formula has been shown by Guggenheim (45) to be quite accurate for argon, and is used here to reduce our value for γ to a temperature of $90\,^{\circ}K$.

To obtain an expression for the temperature dependence of the specific surface energy, we note, that the Gibbs-Helmholtz equation for a plane surface takes the form (17) :

$$u_s = \gamma - T\frac{d\gamma}{dT} \qquad \text{— (9.3)}$$

or, written alternatively,

$$u_s = -T^2\frac{d}{dT}\left(\frac{\gamma}{T}\right) \qquad \text{— (9.4)}$$

Thus, use of the Katayama-Guggenheim formula in equation (9.4) yields

$$u_s = \gamma_0\left[1 + \frac{2}{9}T^*\right]\left(1 - T^*\right)^{\frac{2}{9}} \qquad \text{— (9.5)}$$

where we have used the notation $T \equiv T/T_c$.

Furthermore, from equation (9.2) and equation (9.5), we obtain for the wide temperature range, for which equation (9.2) holds, the ratio of surface tension to specific surface energy as

$$\frac{\gamma}{u_s} = \frac{1 - T^*}{1 + \frac{2}{9} T^*} \qquad -(9.6)$$

Using equations (9.2) and (9.5) to reduce γ and u_s from I24°K we obtain, corresponding to a temperature of 90 °K

$$\begin{aligned} \gamma &= 11.5 \pm 5\% \quad (\text{dynes/cm}) \\ u_s &= 32.4 \pm 4\% \quad (\text{erg/cm}^2) \end{aligned} \qquad --(9.7)$$

These results are compared with previously published values in Table I. . It can be seen, that the agreement of our results with the experimental values is, by comparison, quite satisfactory.

The surface energy found seems still a bit low compared with the experimental reported result, 35 erg/cm^2. It can be noted in passing , however, that, if one uses the rather well established experimental value for the surface tension at 90°K (γ = II.9I dynes/cm) in equation (9.6) , one obtains a value for u_s at 90 °K of 33.5 erg/cm^2 rather than 35 erg/cm^2.

We can now return to the point raised at the beginnig of this section.

In what way do our results for γ and u_s support the view, that the surface structure of our lamina is basically equivalent to that of the "bulk" surface at I24 °K ?

TABLE I The surface tension and the surface energy of argon at 90 K.

	γ dynes/cm	u_s erg/cm^2
Experiment[*]	II.9	35.0
Kirkwood and Buff[22]	I4.9	27.2
Hill[41]	6.0	I9.0
Harasima[**] (free volume theory)		26.4
Corner[36] (free volume theory)	23.I	
Ono[37] ,Kondo and Ono[17] (hole theory)	II.2	25.0
our values obtained here	II.46	32.4

[*] Baly and Donnan :J.Chem.Soc. 8I, 907 (I902) --G.Rudorf:Ann. d. Phys. 29, 75I (I909)

[**] Harasima, A.:Molecular Theory of Surface Thension.In:Advances in Chemical Physics, Vol I(ed.I. Prigogine)Interscience I958

Harasima, A. :Calculation of the Surface Energies of several Liquids.Proc. Phys.-Math. Soc. Japan 22, 825 (I940)

See also (56) for some more values at the Triple Point e.g. γ = II.93 , u_s = 35.4 (adjusted to 90°K)Croxton and Ferrier (56)

The temperature of I24°K ,identifying the state of the free surface, was originally inferred from the mean density found in the interior of the liquid film.The surface tension, which depends implicitely on the molecular of the surface, has now been determined.

We find very reasonable agreement with the experimental value for the bulk surface at I24°K.

The validity of the empirical McLeod equation, thus seems to extend to surfaces of thin films of this nature.

Therefore,either the microscopic structure of our lamina surface(i.e. singlet and pair distributions) is essentially the same as that of the bulk surface between the same densities, - in which case our interpretation of Section 8 can be accepted - or, if it is different, it is distorted in such a way, that the surface tension calculated from it is still the same. One notes, however, that one could simulate a number of laminae of different widths, and at appropriately different kinetic temperatures, which would all show the same interior densities. These would then be expected to all have different configurational structures, while presumably all having the same surface tension, since our particular choice of lamina width and energy does not have anything, particularily distinguishing it from other possible choices.

Rather than contemplating, that - for fixed bulk densities - various different microscopic surface structures can be produced by selecting various laminas of different widths and temperatures, or bulk surfaces at different pressures, all having the surface tension invariant, it seems much more reasonable to accept, that the constant surface tension is just indicative of the invariance of the distribution functions themselves.

This is further illustrated by the agreement found for the surface energy. We can use the values for γ and u_s, determined from the simulated interface, in equation (9.6), to obtain the temperature, at which the ratio of γ and u_s for the macroscopic free surface is equal to the ratio found here. Using our values from equ. (9.1), and solving (9.6), we obtain $T = 124.12\,^{\circ}\mathrm{K}$, in practically exact agreement with the value found from the interior mean density of the lamina.

The closeness of the agreement seems somewhat fortuitous, but the consistency of these results is evident.

SECTION IO

The Density Profile

The microscopic structure of the surface was investigated by attempting to determine the singlet distribution and the pair distribution in this region. Although they are of course intimately related, we will consider these two functions separately in this and the following (Section II.) sections .

IO.I Review of previously reprted Results

Before turning our attention to the results obtained in the present work, we will give a review of the existing knowledge about the density profile for simple liquids.(56)

For this purpose we can recognize three distinct contributions :

i) the experimental evidence

ii) results of " approximate theories ". By this we mean other than strictly statistical mechanics approaches.

iii) results from the distribution function approach of statistical mechanics

If one perhaps excludes the critical region, one has to note, that little direct information on the surface structure of simple liquids has been obtained from experiment. Indirect evidence, however, obtained from studies of the dependence of the surface tension on the radius of curvature, small droplets, liquid metals, to name but a few, has long been taken to indicate, that the interfacial region should, for temperatures below the critical point, be very narrow - of the order of a few intermolecular distances (17)

Details about the form taken by the density change in this microscopic region have been first obtained from a quasi-thermodynamic approach by Hill (41). The method uses an integral equation, derived from the constancy of the chemical potential across the phase boundary, to calculate the density profile. These profiles were obtained by Hill for various temperatures and are shown Fig. 6

The for many years only other density profiles at these temperatures, were those obtained by Ono and Kurata (37,38) from the "hole model". These curves show essentially the same shape as the profiles of Hill, and the basic equivalence of both methods has been pointed out by Kondo and Ono (17)

In both cases, the density changes monotonically from liquid to vapour. It is however a point of contention, as pointed out earlier, to what extent information on the microscopic structure, can be obtained from these approaches .

FIG. 6

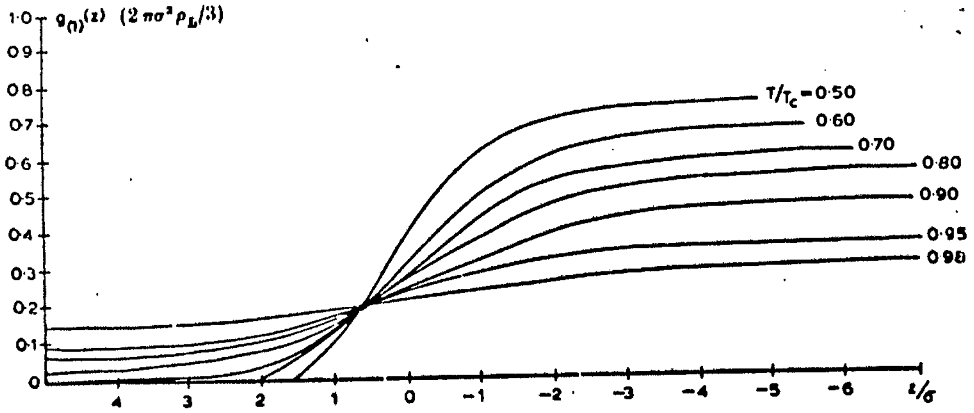

Fig. 6 : Density profile obtained by Hill(41) from quasi-thermodynamic theory.

(Figure taken from (56))

More recent is the development of a method by Toxvaerd (62), which is based on the perturbation theory of Zwanzig (70), Barker and Henderson (71). For a square-well liquid Toxvaerd obtains a monotonic density profile through the surface .

The distribution function approach of statistical mechanics has during the last twenty years formed the theoretical basis for most of the information gained about the microscopic structure of dense fluids. It has in the most recent years also been applied to the liquid surface, and approximate forms of the density profile have been obtained.(56)

The integral equation most suitable for this purpose, is the Born-Green-Yvon-Bogolubov integro-differential equation of the lowest order, which is an exact equation linking the singlet and the pair distribution functions:

$$kT\, \nabla_1 n^{(1)}(\underset{\sim}{r}_1) = -\int \nabla_1 \psi(\underset{\sim}{r}_{12})\, n^{(2)}(\underset{\sim}{r}_1, \underset{\sim}{r}_2)\, d\underset{\sim}{r}_2 \qquad -(10.1)$$

$\psi(\underset{\sim}{r}_{12})$ is the interaction potential (assumed to be "pair-wise", k is Boltzmann's constant and T the temperature. (∇_1 indicates the gradient with respect to $\underset{\sim}{r}_1$)

By writing

$$n^{(1)}(\underset{\sim}{r}_1) = n_l\, g^{(1)}(\underset{\sim}{r}_1) \qquad -(10.2)$$

and

$$n^{(2)}(\underset{\sim}{r}_1, \underset{\sim}{r}_2) = n_l^2\, g^{(1)}(\underset{\sim}{r}_1)\cdot g^{(1)}(\underset{\sim}{r}_2)\cdot g^{(2)}(\underset{\sim}{r}_1, \underset{\sim}{r}_2) \qquad -(10.3)$$

(where n_ℓ is the density of the liquid phase) , we can re-write equation (10.1) as

$$kT \nabla_1 g^{(1)}(\underset{\sim}{r}_1) = - n_\ell \, g^{(1)}(\underset{\sim}{r}_1) \int \nabla_1 \psi(\underset{\sim}{r}_{12}) \, g^{(1)}(\underset{\sim}{r}_2) \, g^{(2)}(\underset{\sim}{r}_1, \underset{\sim}{r}_2) \, d\underset{\sim}{r}_2 \qquad -(10.4)$$

The density profile is defined by the function $g^{(1)}$ which is to be obtained as a solution of equation (10.4). The problem lies in the fact, that in the integrand, the function $g^{(2)}$ is not known in the surface zone, and the need arises at this stage, to choose a suitable approximation for the pair distribution in this region.

The work of the various authors, who have used equation (10.1) to obtain density profiles, is thus characterized by the different approximation used for $g^{(2)}$. (56) (Jouanin 1969(57), Toxvaerd 1972/73(62,58),Croxton and Ferrier 1971(59,60), Nazarian 1972(61)). Usually, some kind of interpolation between the RDF's of the two phases was employed.

Two different approximations used by Nazarian(61) were

a)
$$\begin{aligned} g^{(2)} &= g_\ell^{(2)}(r) \quad \text{if} \quad z_1 + z_2 < 0 \\ g^{(2)} &= g_v^{(2)}(r) \quad \text{if} \quad z_1 + z_2 > 0 \end{aligned} \qquad -(10.5)$$

Where $g_\ell^{(2)}$ and $g_v^{(2)}$ are the radial distribution functions in the interior liquid and vapour phases, and $g_v^{(2)}$ was in turn approximated by

$$g_v^{(2)}(r) = \exp(-\psi(r)/kT) \qquad -(10\cdot6)$$

and the location of the equimolecular dividing surface is at z =0 .

Secondly,

b)

$$g^{(2)}(z_1, z_2, r_{12}) = g_{\ell}^{(2)}(r_{12}) + \left[\frac{z_2}{z_{12}} A(z_2) - \frac{z_1}{z_{12}} A(z_1)\right] \times \left(g_{v}^{(2)}(r_{12}) - g_{\ell}^{(2)}(r_{12})\right) \qquad -(10.7)$$

where A is the unit step function.

For both these approximations Nazarian has obtained density profiles for argon at 90°K, and both curves show a very strongly oscillatory character .(Fig. 7)

A different form of interpolation between the bulk RDF's has been used by Toxvaerd(58) by assuming

$$g^{(2)}(r_1, r_2) = \alpha\, g^{(2)}(r_{12}; n^{(1)}(r_1)) + (1-\alpha)\, g^{(2)}(r_{12}; n^{(1)}(r_2)) \qquad - \quad (10{\cdot}8)$$

$g^{(2)}(r_{12}; n^{(1)}(r))$ indicates the RDF appropriate for a constant density equal to the value of $n^{(1)}$ at r .These density dependent RDF's are themselves in turn approximated as linear interpolations between the RDF's of the liquid and the vapour phases. Selfconsistent solutions for $g^{(1)}$ are obtained for one value of α only for each fixed temperature by iteration of equation (10.1). The results show <u>monotonic</u> density profiles, in contrast to the results of Nazarian (61).

FIG. 7

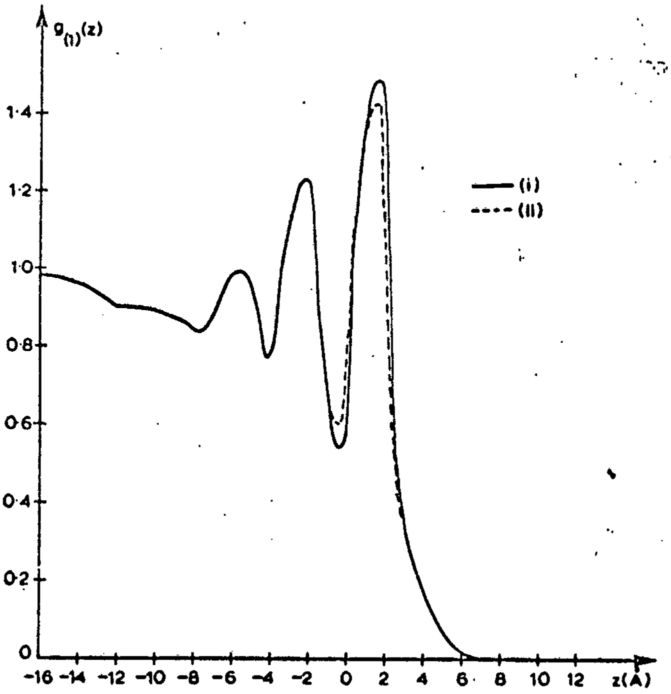

Fig. 7 : The density profiles(for 90°K and argon) obtained by Nazarian(61) by employing two different approximations. (taken from (56))

FIG. 8

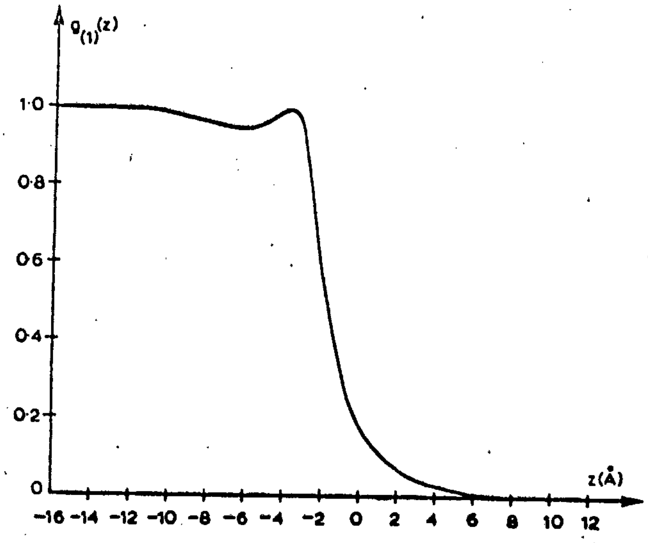

Fig. 8 : Density profile obtained by Croxton and Ferrier (59)(Taken from (56))
This profile refers to the triple point of argon.

A somewhat different method of obtaining $g^{(1)}$ from the equation has been employed by Croxton and Ferrier (59,56) These authors have used a constant, isotropic RDF for $g^{(2)}$, and have tried to account for the effect of the anisotropy of the surroundings in the surface, "felt" at $\underset{\sim}{r}$, by changing the interaction through the inclusion of an operator, which is in effect a z-dependent function multiplying $\psi(r_{12})$. The density profile obtained in this way for argon at the triple point, is again of a non-monotonic character(Fig. 8), although not showing such extreme oscillations, as those obtained by Nazarian (61)

We can therefore summarize the existing position as follows :

Various forms of the density profile have been obtained. The most important question, around which most interest is centred, is at the moment, whether or not density profiles, of an oscillatory, non-monotonic form do exist, even for simple liquids like argon. If this is the case, it can be assumed all the more, that the surface structure of liquid metals could have this oscillatory character.

Results related to quasi-thermodynamics seem to show monotonic profiles, but it seems unlikely that these approaches could show microscopic features like these oscillations anyway.

Statistical mechanical derivations, on the other hand, have yielded non-monotonic profiles, though not for all methods (e.g. Toxvaerd (58)). Furthermore, non-monotonic solutions do not show consistency about the magnitude and the extent of the oscillations.

The evidence for the existence of oscillatory profiles provided by the 2-dimensional MD calculation (66), is weakened by the fact, that oscillatory forms are more likely to exist in two-dimensional models than in three-dimensional ones.

Our next step is now,to consider the profile obtained in the present work.

10.2 The Density Profile obtained in the Present Work

It has been noted already, that the simulation of the liquid surface requires an particularily large amount of computer time, because of the need to average for very long periods, before statistically significant results are obtained. We have indicated, that this difficulty imposes restrictions on the resolution with which distribution functions could be determined in the present work.

The problem is particularily critical here, since it is exactly the question of whether stable density oscillations are indicated by the profile, which is of most interest, and because of the need to distinguish these oscillations from the remaining statistical fluctuations. The best approach would be,of course, to simply continue the simulation , until these questions can be answered with certainty, but unlimited computer time can of course not be available.

In the light of these remarks, the need is felt, to approach the interpretation of the results obtained here for the density profile, with some care, and to proceed from higher levels of confidence(i.e. in the results) to those of lower confidence in a systematic way.

We will thus first consider the obtained density profile at a resolution of 2 Å , try to see what information can be gained from this, and then consider the (same) profile function for resolutions of I Å and ½ Å.

The density profile through the liquid surface of argon at (effectively) I24 °K is shown in Fig.9 ,plotted for a resolution of 2 Å. For this, the statistical significance of the curve can be accepted with considerable confidence. Evidence for this is provided by :

i) Analysis of the behaviour of individual values(i.e. at certain definite points) during the averaging process.

ii) The other surface of the lamina has a similar shape

iii) The smoothness of the curve.

The following features of the profile can be noted :

i) The density change is accomplished over a distance of about I5 Å.

FIG. 9

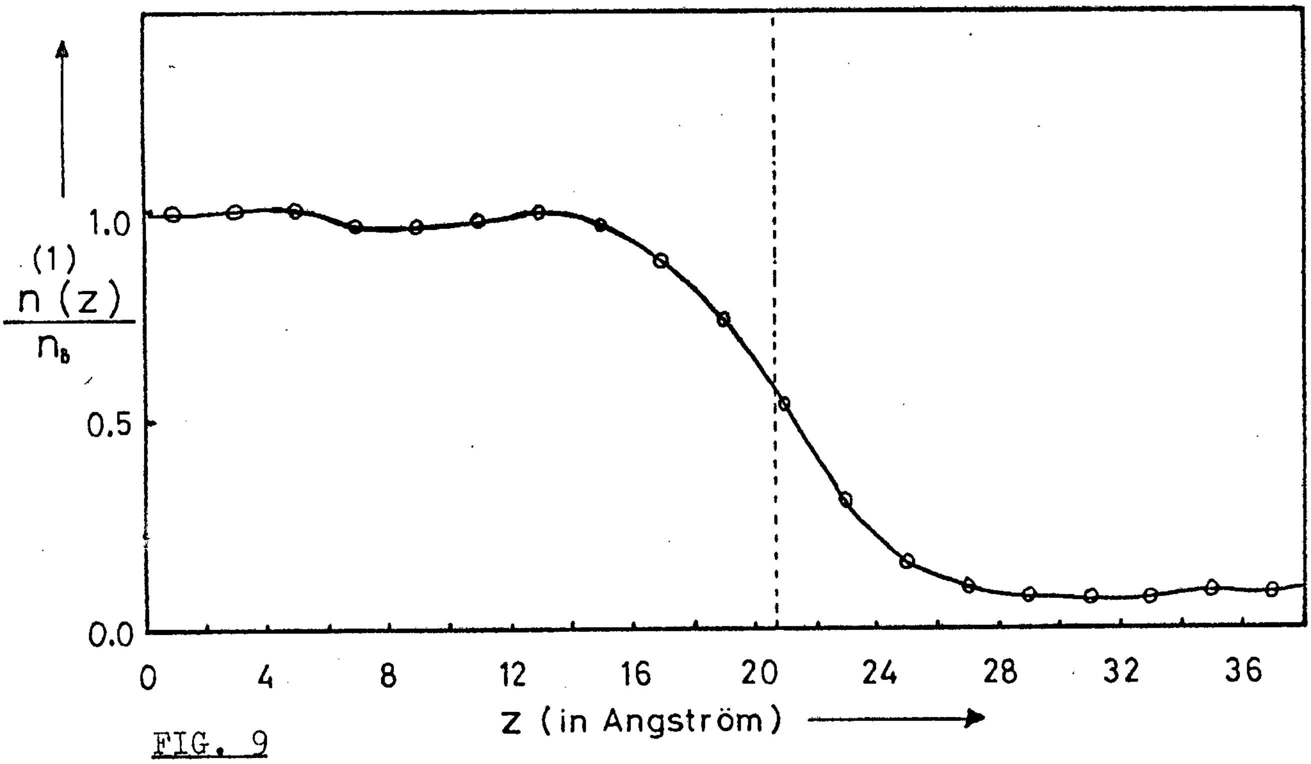

FIG. 9 :The density profile through the surface.n_B is the mean number density in the interior of the liquid film and was taken as I.675 xI0^{-2} atoms/Å^3 (I.I2 gm/cm^3).The vertical broken line indicates the position of the equimolecular dividing surface(±0.3 Å)

(2 Å - resolution)

ii)The general shape of the profile seems similar to that of the functions obtained by quasi-thermodynamics by Hill(41)(also those of Ono and Kurata(37,38))

iii) A deviation from the monotonic form of the profile is shown by the depression near $z = 9$ Å. This is small in magnitude, but should be accepted as significant[*]. Our profile refers to the rather high temperature of I24°K, and any deviations from monotonic form must be expected to become progressively less pronounced as the critical point is approached.

At this (relatively highest) level of confidence, we can therefore conclude, that, even for argon at I24°K , the profile is not strictly monotonic. The existence of this small oscillation at this temperature, makes it seem unlikely, that the oscillatory nature of solutions obtained theoretically for lower temperatures, should be just a spurious effect, due to the approximations involved in the method of calculation.[**]

Whether the density profile at I24°K has precisely the form shown in Fig.9 , or whether density oscillation of "wavelength" smaller than 2 Å are present, can of course

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[*] At an intermediate stage of the calculation, this was in doubt, but has now been established by method i)above.

[**] It may of course still happen, that a method of calculation, which, because of approximations involved,will only yield smooth profiles as results, shows oscillatory forms for earlier iterates (e.g. Toxvaerd(58) ??)

FIG. IO

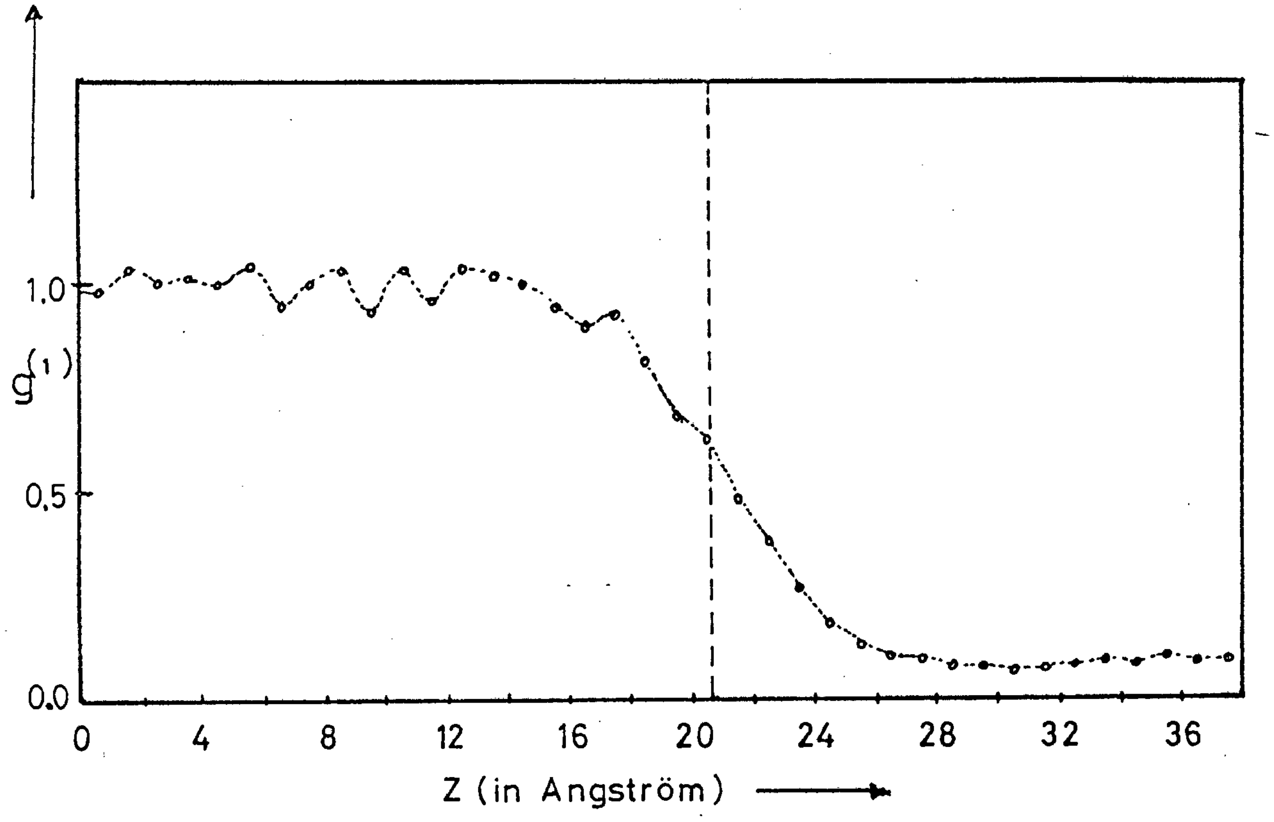

Fig. IO : Density Profile through the surface. This curve was plotted with I Å resolution and clearly shows oscillatory character. Uncertainty in individual values is approximately ±0.0I5 .

not be decided from the 2Å-resolution curve in Fig.9 .

I Å resolution

The same density profile as in Fig.9 , but using our measured values to resolution I Å, is plotted in Fig10 The individual points in Fig.9 are in fact simply averages over pairs of neighbouring values in Fig.10 .

This curve seems to indicate, that our use of 2 Å resolution, has indeed suppressed an existing density oscillation of shorter repitition length. It is felt, that the variations shown in the I Å -curve, are not due to remaining statistical fluctuations. This opinion has been reached on the following grounds :

The existing statistical fluctuations for a few individual values in the I Å curve were monitored(e.g. for the average values at z = I7.5 Å and I6.5 Å). The remaining uncertainties in individual values were found be still large, about ± 0.015 , but clearly smaller than the height of the "peaks"and"troughs" of the oscillation.

It is also evident, that the curve is quite smooth in the lower density region (i.e. beyond z =22 Å, say). Any statistical fluctuation should, however, be much more pronounced (for a longer time) for low densities, than for the higher density part on the liquid side.

Although individual values of the peaks and troughs are not obtained with great accuracy (± 0.015), we therefore reach the conclusion, that the singlet distribution for our temperature, does seem to show definite oscillatory character of the form indicated in Fig.10 .

The "amplitude" of these oscillations is not very large here, but whether the oscillations might, for 90°K, reach the extreme forms shown in the solutions of Nazarian (Fig. 7 (61), can not be decided from our results.

One may speculate, however, whether the similarity between our 2 Å-curve(Fig.9), and the profile calculated by Croxton and Ferrier for the <u>triple point</u>(Fig 8. (59 ,56)), which was presumably calculated with far better resolution, may not be indicative of a systematic suppression of structural detail inherent in Croxton and Ferrier's method.

SECTION II

The Pair Distribution Function in the Surface

Our investigation of the pair distribution $n^{(2)}$ in the surface zone will, as has been indicated already in Section 7 , take the form of an investigation of the function $g^{(2)}(z_1,\varphi,r)$, defined by

$$n^{(2)}(\underset{\sim}{r}_1,\underset{\sim}{r}_2) = n_\ell^2\, g^{(1)}(z_1)\cdot g^{(2)}(z_2)\, g^{(2)}(z_1,\varphi,r) \quad -\ (11.1)$$

By thus separating* the "direct" and the "indirect" effect of the density profile in $n^{(2)}$, it is hoped to gain insight into the structure of the surface structure more easily.

Very little seems to be known about the function $g^{(2)}$ in the interfacial region.

It has been mentioned before already, that various authors have approximated $g^{(2)}$ in the surface by different forms of linear combination of the liquid and vapour RDF's, to calculate thermodynamic quantities or, more recently, to obtain the density profile from the BGYB-equation. Such a scheme can in a sense, be of course considered as an indirect investigation of the PDF in the surface, but, as noted before, successful calculation of γ and μ_s in this way, does not necessarily imply the realism of the approx-

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* The separation is of course mostly formal.

imate form of $g^{(2)}$. The conclusion about $g^{(2)}$, which can perhaps be drawn from these calculations is, that one would not expect $g^{(2)}$ in the surface to be radically different from the interior phase form.

The following direct investigations of $g^{(2)}$ in the surface have been reported.

Croxton and Ferrier (64) have investigated the angular (i.e. φ -) dependence of $n^{(2)}$ for the plane argon surface, albeit in a somewhat restricted form : assuming no radial distortion in $n^{(2)}$ they write (56)

$$n^{(2)}(z,\underset{\sim}{r}) = n_\ell^2\, g_\ell^{(2)}(r)\, A_{00}^2(z)\left[P_0^0(\cos\varphi) + \lambda(z) P_1^0(\cos\varphi)\right]^2$$

<u>i.e.</u>

$$n^{(2)}(z,\underset{\sim}{r}) = n_\ell^2\, g_\ell^{(2)}(r)\, A_{00}^2(z)\left[1 + \lambda(z)\cdot\cos\varphi\right]^2 \qquad - \quad (11.2)$$

Using this $n^{(2)}$ to minimize the free energy in the surface, they obtain the functions A_{00}^2 and $\lambda(z)$ for different temperatures. We will comment on these results further below. Croxton (56) also reports an investigation of the radial distortion of $g^{(2)}$ in the surface via the Smoluchowski equation. This work has not been published at the time of writing, but Croxton reports in his review article(56) the result, that the radial distortion of $g^{(2)}$ was found to be negligible. This, however, does not seem to be borne out by the results of the present investigation.

In the absence of much detailed existing information on $g^{(2)}$ in the surface region, the most suitable approach seems to be, to compare this function directly with the

RDF of the liquid interior.

In the present investigation, $g^{(2)}(z_1, \varphi, r)$ has therefore been obtained as a series of "radial" distribution functions, restricted to a number of dicrete z_1-values and a few different directions.

Information about the structure of the surface zone is contained in abstracted form in the $g^{(2)}$-functions. The interpretation of a pair distribution function in the form of a mental picture of the three-dimensional arrangement of molecules can, even for the isotropic RDF in the interior of a liquid, be done only in terms of the major features of these functions, like the "first peak","first trough", the "second peak" and so on. To interpret physically in this way the finer details of such a function explicitly, does not seem feasible for the isotropic case, or, a forteriori, for the anisotropic situation we are concerned with here.

The ideal would be, to use our "measured" data to obtain a mathematical expression for $g^{(2)}$in the surface. This, however, has not been possible, because of the small number of discrete z_1-locations and directions for which $g^{(2)}$was obtained. Instead, we will exhibit the various "radial" functions, observe the deviation from the RDF of the interior in these curves, and attempt to recognize some general trends in the form this distortion takes for different z_1-positions and directions. To this extent our information is therefore only qualitative in nature.

FIG. II

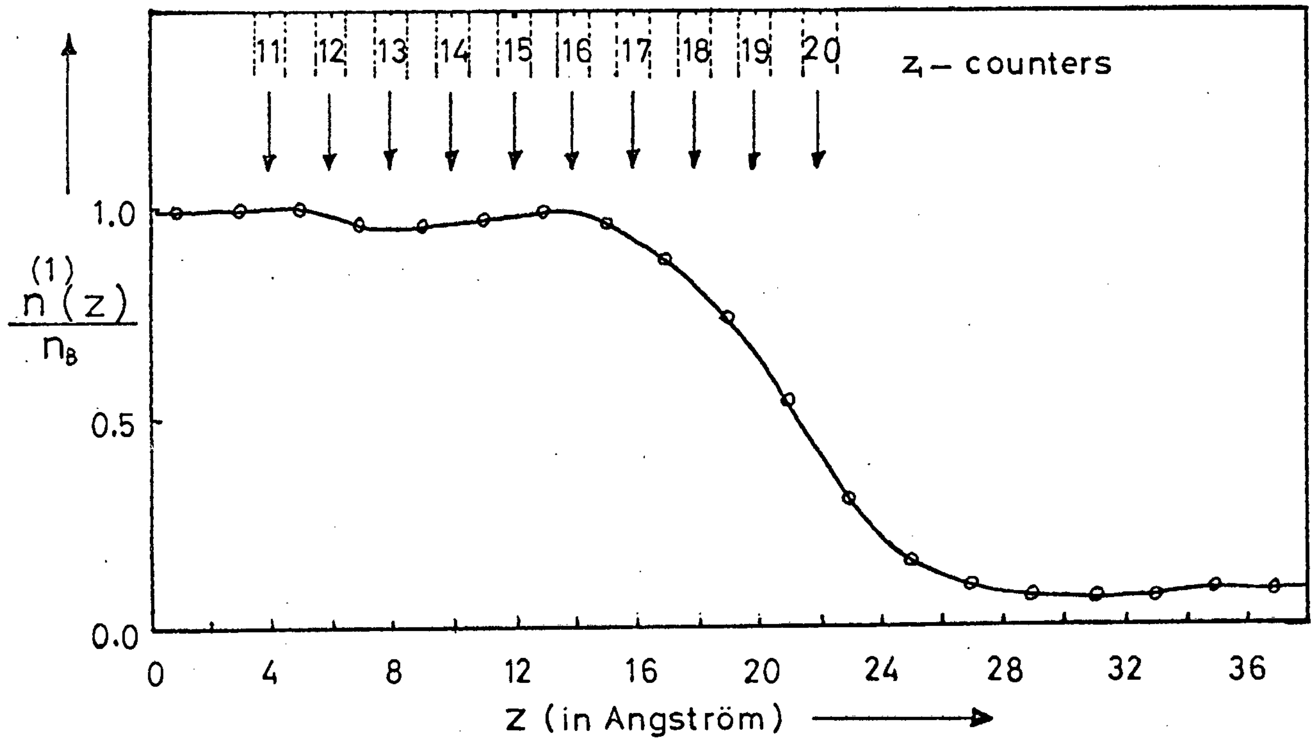

Fig. II :

:The diagram indicates the various z_1-positions used. The curves in FIG. I2 to I7 are identified by the appropriate z_1 counter numbers II to 20 .

In order to simplify this task, we will now only consider the following three distinct directions :

i) normal to the surface, "outward" directed from liquid towards vapour phase, called the F-direction in the graphs,

ii) parallel to the surface - the Q-direction, and

iii) an intermediate direction at 45° to the positive z-axis - called the S-direction .

Thus the different functions can be viewed as RDF's about molecules having z-coordinates equal to z_1 (plus or minus $\frac{1}{2}$ Å). The locations of these z_1-values are indicated in Fig.11 and are used to identify the various curves , which are shown in Fig.(12–14) together with the RDF obtained for the interior lamina.

These curves have been obtained by averaging for a period of 87 ps, at 1 ps intervals. To provide some indication of the statistical significance, i.e. about the extent of remaining statistical fluctuations in these curves, some of the same functions are shown after 72 ps of averaging in Fig 15–17 .

We will now make a few remarks about these graphs :

I. The F-direction

Of the ten z_1-positions used for the surface (Nos. 11 to 20), only those numbered 11 to 17 have been used in Fig.12 . Since the F-direction is normal to the surface,

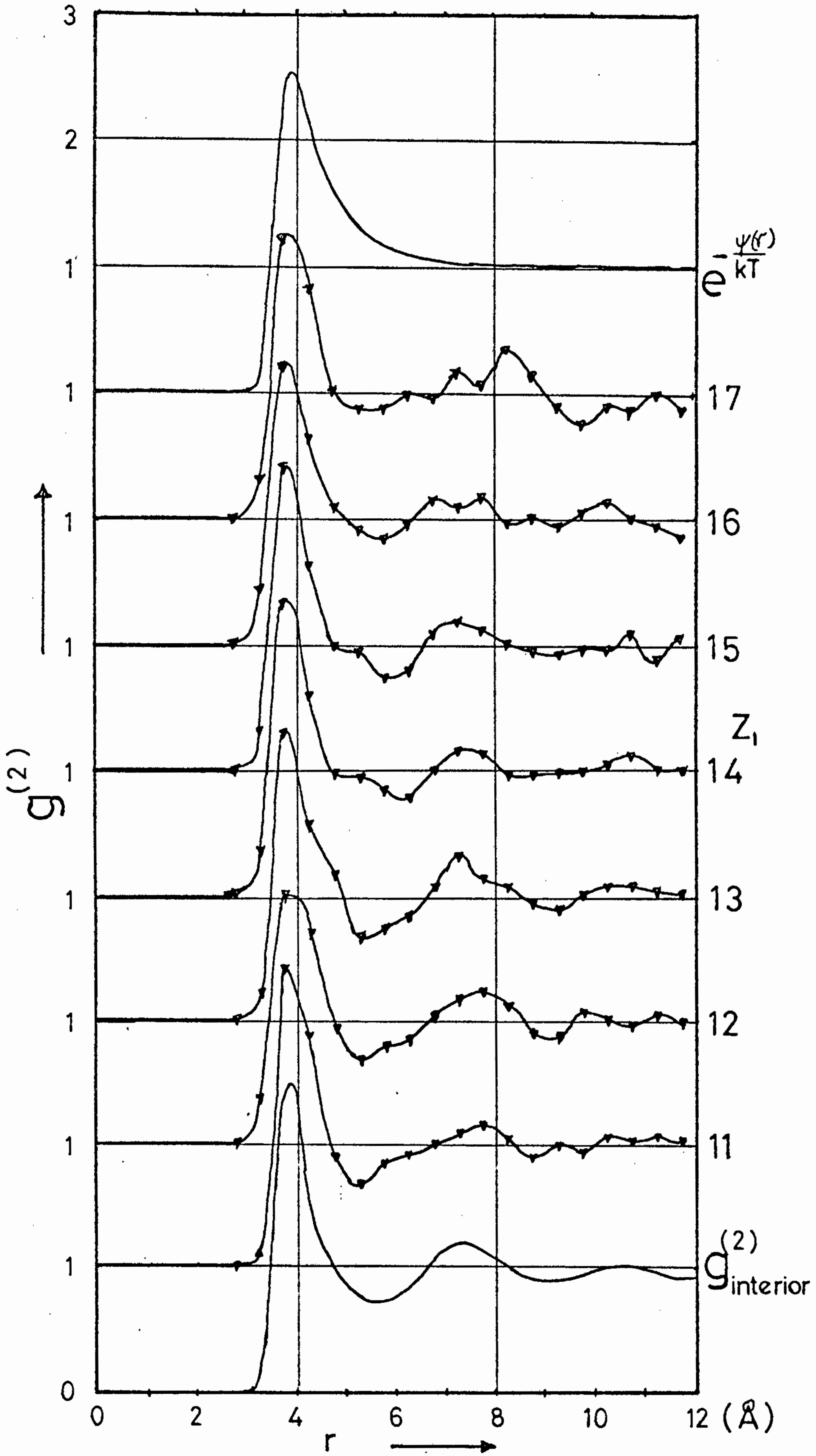

FIG. I2 : Pair distribution functions in the F-direction are shown, together with the RDF of the interior lamina and an approximate form for the gas phase. These curves are averages over 87 ps.

the three outer curves I8,I9,20 reach far into the vapour phase and have not yet reached a satisfactory degree of significance.

We note the following features :

The position of the First Peak seems unchanged. This must be expected from the steepness of the interaction potential.

The First Trough shows a systematic change as we progress through the surface. Even curves II and I2 show an unsymmetrical First Trough, somewhat different in shape from the form shown in the interior RDF.

Reference to Fig.10 indicates, that these curves actually cover the oscillatory part of the profile.

The unsymmetrical shape of the First Trough changes systematically as we move through the surface zone : while the lowest point first seemed shifted inwards, it now appears to move outwards until the asymmetry seems "reversed".

The change between the two shapes seems to occur somewhere between curves I3 and I4. Considering the z_1-positions of these curves in Fig.9 , one notes that the trough corresponds to material near the"shoulder"of the profile. The small "hump" at about r =5 Å developing in I4 and I5, and which seems to be "anticipated" in I3 at the outer slope of the First Peak, apears to be somehow associated with the beginning oscillations in the profile in this region. The First Trough seems to become generally more shallow as one passes further to the

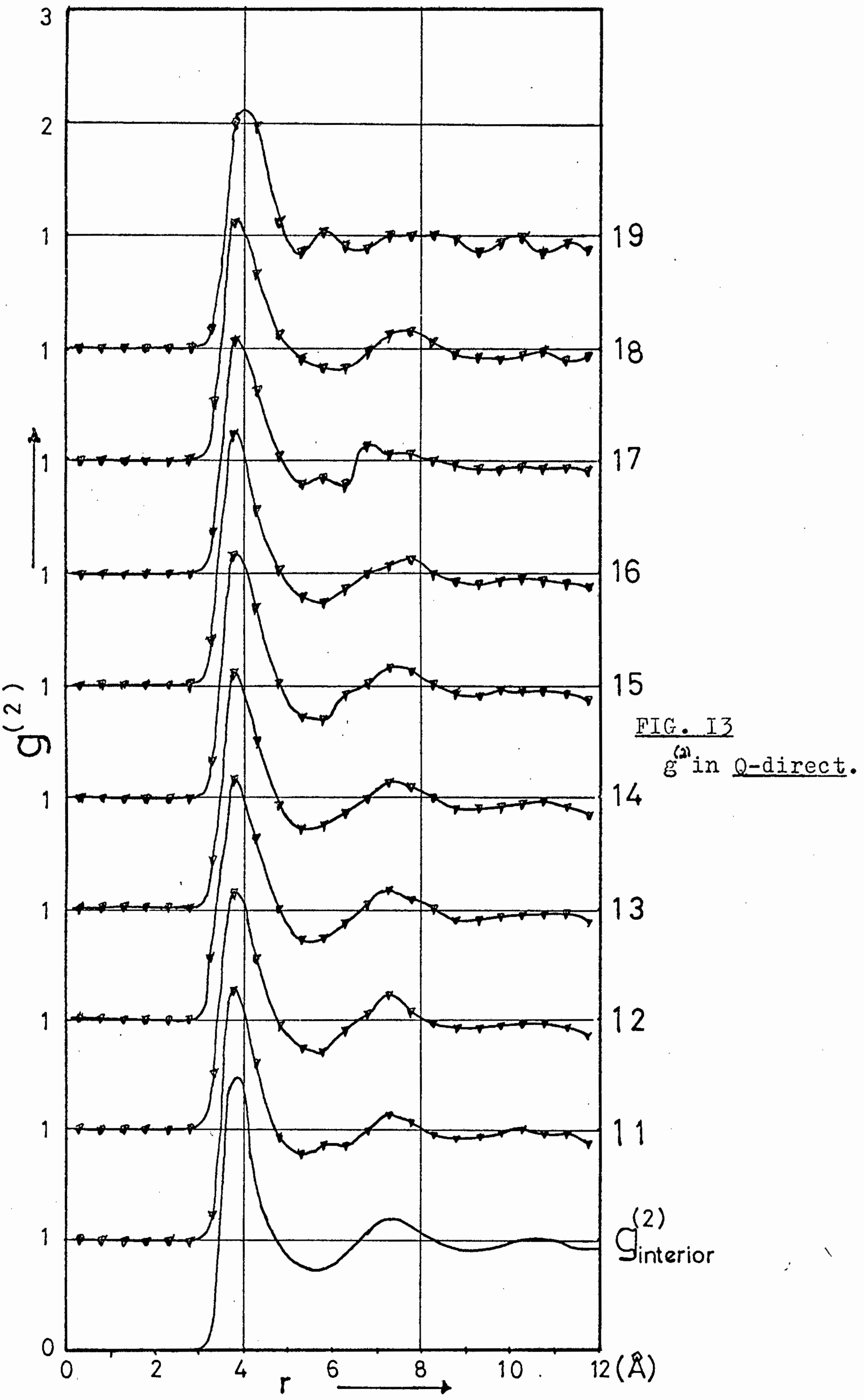

FIG. I3 : g in Q - direction (87 ps). z_1-counter nos. II→I9 low density region - as might be expected .

The Second Peak also shows change of shape, shift in position and seems to be breaking up into two distinct peaks.

The pronounced trough at about r = 9.75 Å in curve I7 seems surprising, since this position refers to a very low density already. If due to a fluctuation, however, this would have to be a very persistent one, since comparison with the F-I7 curve in Fig.15 shows, that it has not much changed during the last I5 ps (i.e. from 72 ps to 87 ps). It thus would have either have had to have lasted for a long time (or be measured very often) during the first 72 ps, or must have persisted during much of the last I5 ps. (Some other parts of curve I7, for larger r ,seem quite a bit changed)

The function $\exp(-\psi(r)/kT)$, which may be taken as a approximation of the RDF in low density gas phase, has also been included for comparison.

2. The Q-direction (parallel to the surface)

Curves II to I9 are shown in Fig.13 (averages over 87 ps), and some of the curves after 72 ps are plotted in Fig.16 .

Most noticable feature is the change in the shape of the First Trough, which is rather similar to the change observed for the F-direction. It is interesting to note

FIG. I4

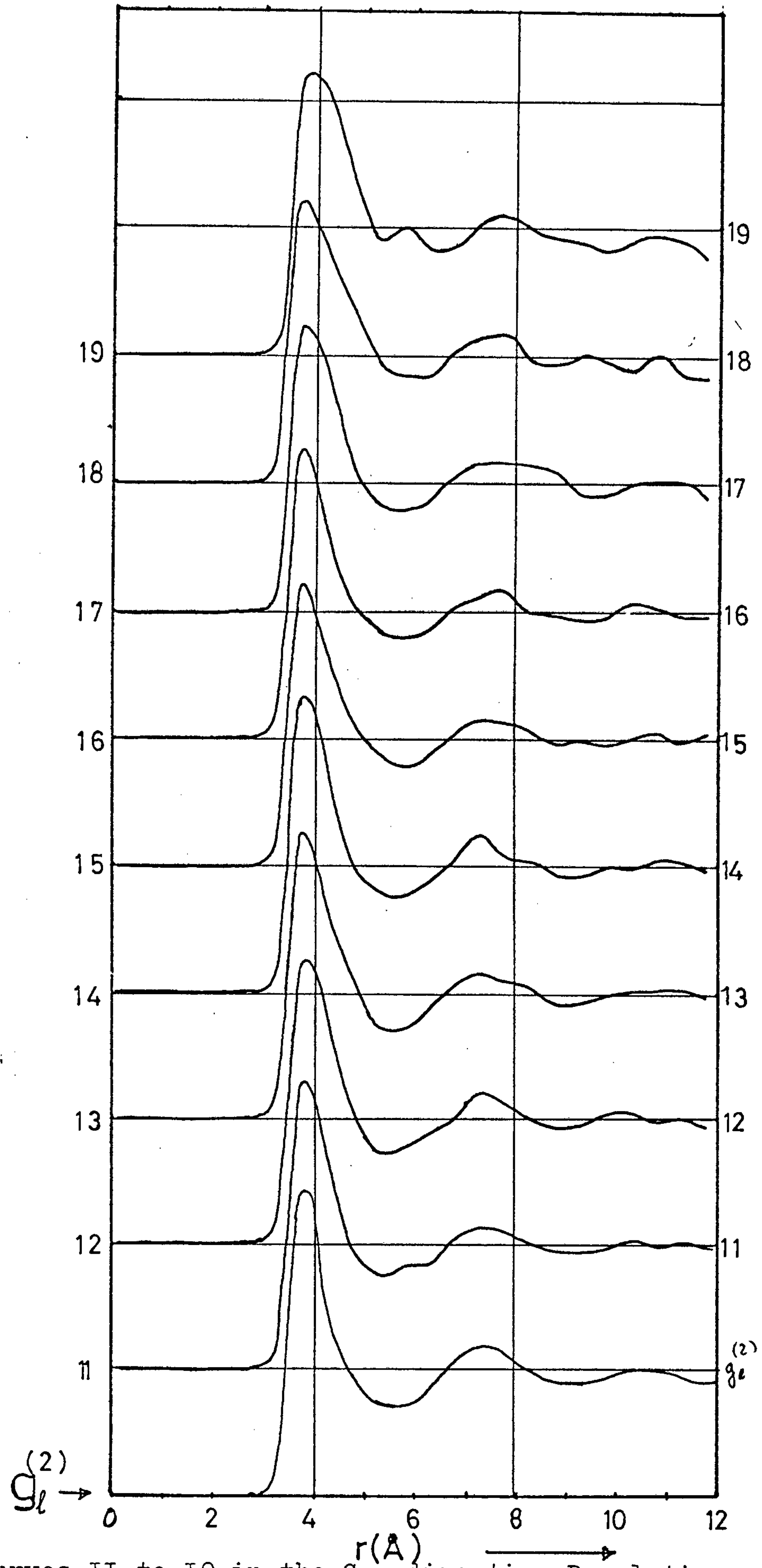

Fig. I4 : Curves II to I9 in the S - direction. Resolution is, as before, ½ A.

this similarity for the two directions which are at right angles to each other. The change-over from the one to the other type of shape of the First Trough, happens between curves I6 and I8. Curve I7 in between seems curiously distorted, and one notes, that the whole curve I7 now refers to the "shoulder " of the profile, where the "first" strong oscillation (peak at $z = I7.5$Å, trough at about I6.2 Å, Fig10) will be included in the volume sampled.

The slope on the outer side of the First Peak appears to become smaller (in absolute terms) as one passes towards lower density (c.f. function $\exp(- \psi(r)/kT)$)

3. The S-direction

Curves II to I9 are shown in Fig.14 (87 ps) and some are plotted in Fig.17 (for 72 ps).
These functions show similar features as the Q-curves. The same change of shape of the First Trough is evident, but there are three intermediate curves showing a symmetrical First Trough. The absolute decrease in the slope on the outer side of the First Peak can again be seen. This seems to be a phenomenon generally associated with a decrease in density.

A curious phenomenon is seen in connection with the Second Peak of these S-curves. One notes, that alternate curves (i.e. differing in their z_1-positions by 4 Å) show similarities in their Second Peaks : Curves I2,I4,I6, I8 show a more peaked shape for this, I2 and I4, and I6,I8

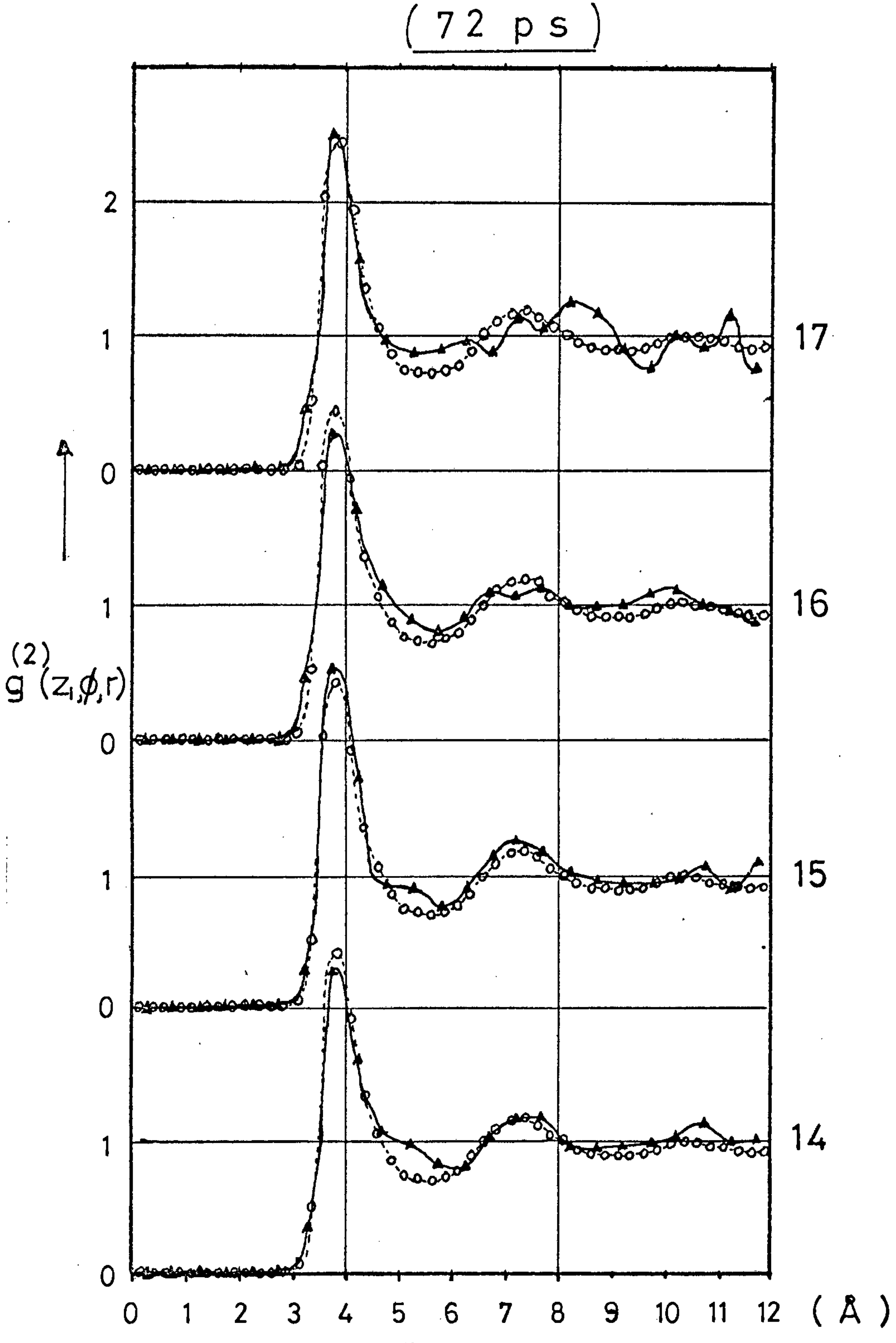

FIG15 :Some pair distribution function in the surface zone.For these curves the direction is normal to the surface(F-direction) Curves are identified by their z_1-counter numbers on the right hand side(-▲-▲-▲).The broken line curves represent the radial distribution function of the interior liquid.(-○--○---○)

FIG. I6

(AVERAGES FOR 72 ps)

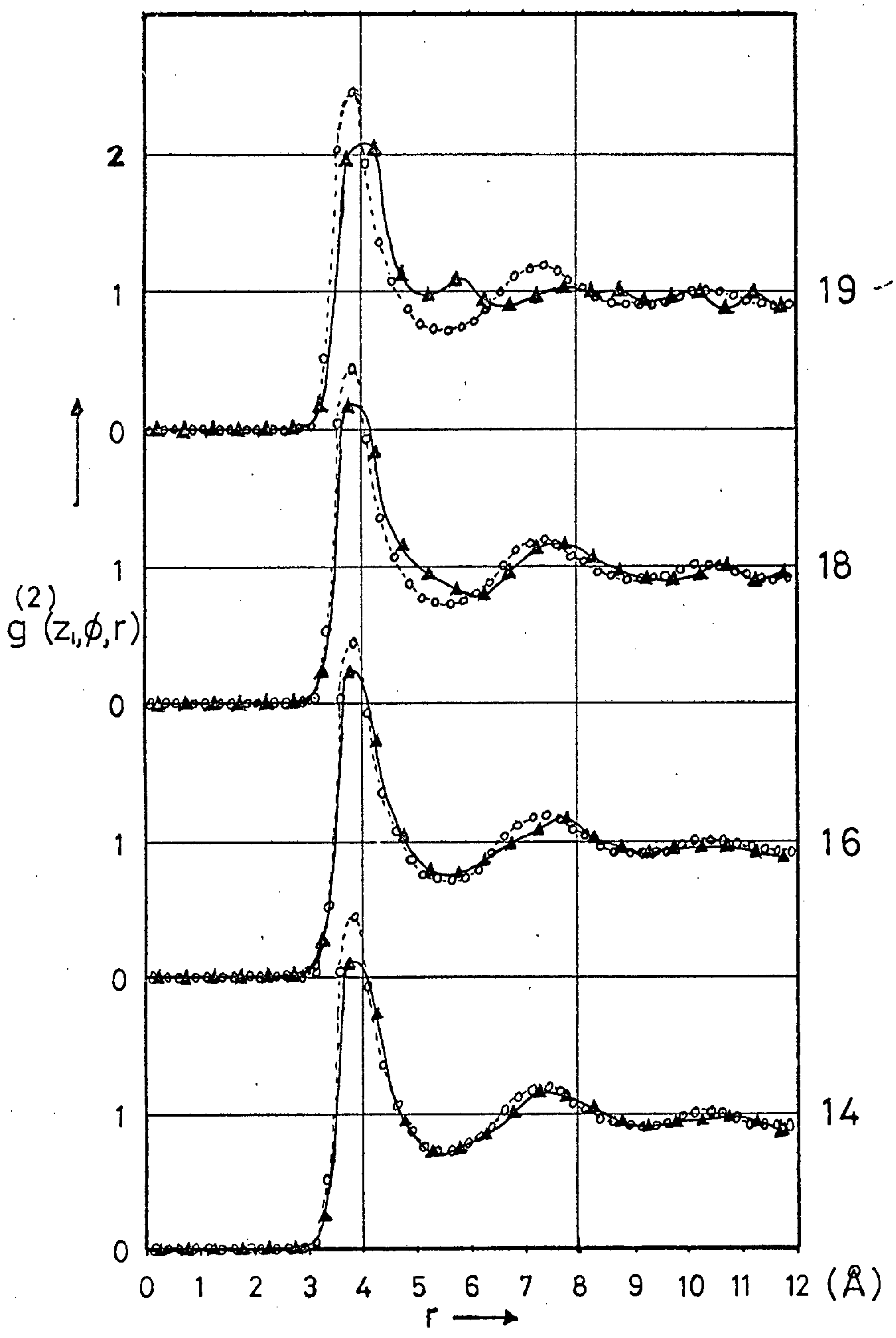

FIG I6:Some pair distribution functions of the interface in the Q -direction(parallel to the surface) are compared with the radial distribution function of the interior.(Notation as FIG 15

FIG. I7

AVERAGES FOR 72 ps

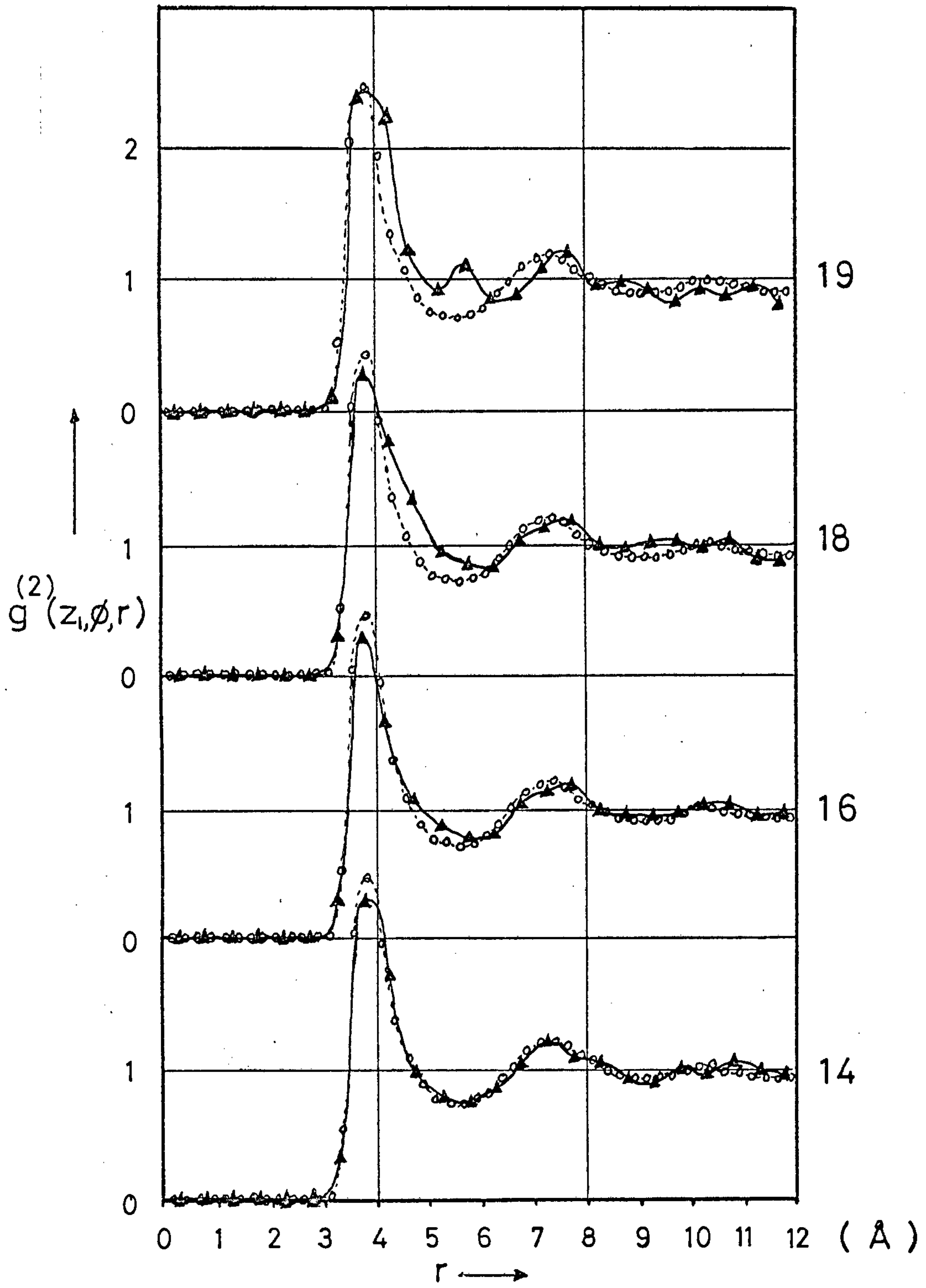

FIG I7: Pair distribution functions of the surface region in the S-direction (45° to z-axis) are compared with the radial distribution function of the interior liquid. (Notation similar to FIG 15 being respectively almost identical.

Likewise, curves I3,I5,I7 have a Second Peak of a different, broader shape, those of I3 and I5 being practically identical. The probability of these similarities being brought about by chance, seems rather small, but no satisfactory explanation seems to be at hand. The z_1-positions defining these curves are located in the oscillatory part of the profile, but no obvious relation with the curious 4Å-periodicity can be seen.

The information, which can be obtained from these curves, can perhaps be summarized as follows :

Compared to the interior RDF, the pair distribution function in the surface seems to be radially distorted to an appreciable degree. This distortion is already noticable for the oscillatory part of the transition zone and is seen to follow a systematic pattern, as one passes through the surface, which, however, is not of a particularilу simple form in its details.

For the same z_1-position, curves associated with different directions show a surprising degree of similarity, but there are also obvious differences.

Our results do not seem to confirm the result quoted by Croxton (65), that the radial distortion in $g^{(2)}$ is minimal.

Our results are not easily related to the investigation of the dependence of the pair distribution in the surface by Croxton and Ferrier (64), since it is the function $n^{(2)}$ which is investigated by these authors. Since they assume an"undistorted" $g^{(2)}$, and since the function $g^{(1)}$ multilpying $g^{(2)}$in $n^{(2)}$would suppress most of the detailed features of $g^{(2)}$beyond the first peak anyway, the angular effect investigated by these authors seems to be mainly due to the density profile $g^{(1)}$ itself.

Some general remarks

Our method of using a lamina of finite width,seems to provide a suitable means for the investigation of the plane surface. Most obvious possible improvements would include the use of a somewhat faster integration routine which would make it possible to use a lamina of greater width, or to obtain results with greater accuracy.

In the present work, we have been concerned only with"equilibrium"properties, but the basic method used here seemes equally suitable for a determination of time-dependent correlation functions in the surface. The effect on the finite width of the lamina, on these quantities would, however, have to be assessed first.

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