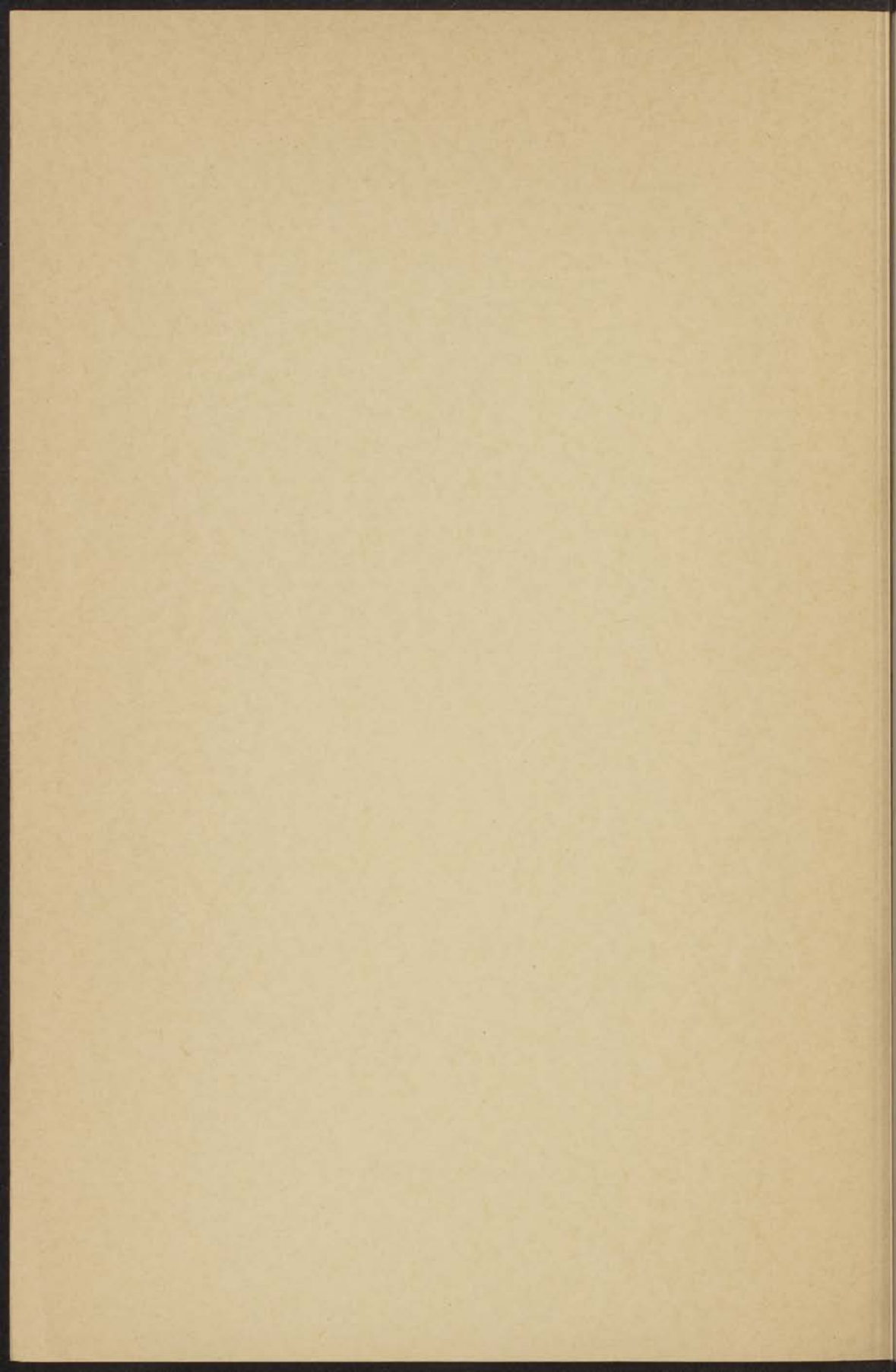


Tjerk

TWO INVESTIGATIONS ON HELIUM
AT LOW TEMPERATURES

H. H. TJERKSTRA



Hoogleraar
Dr. J. J. HERMANS

TWO INVESTIGATIONS ON HELIUM AT LOW TEMPERATURES

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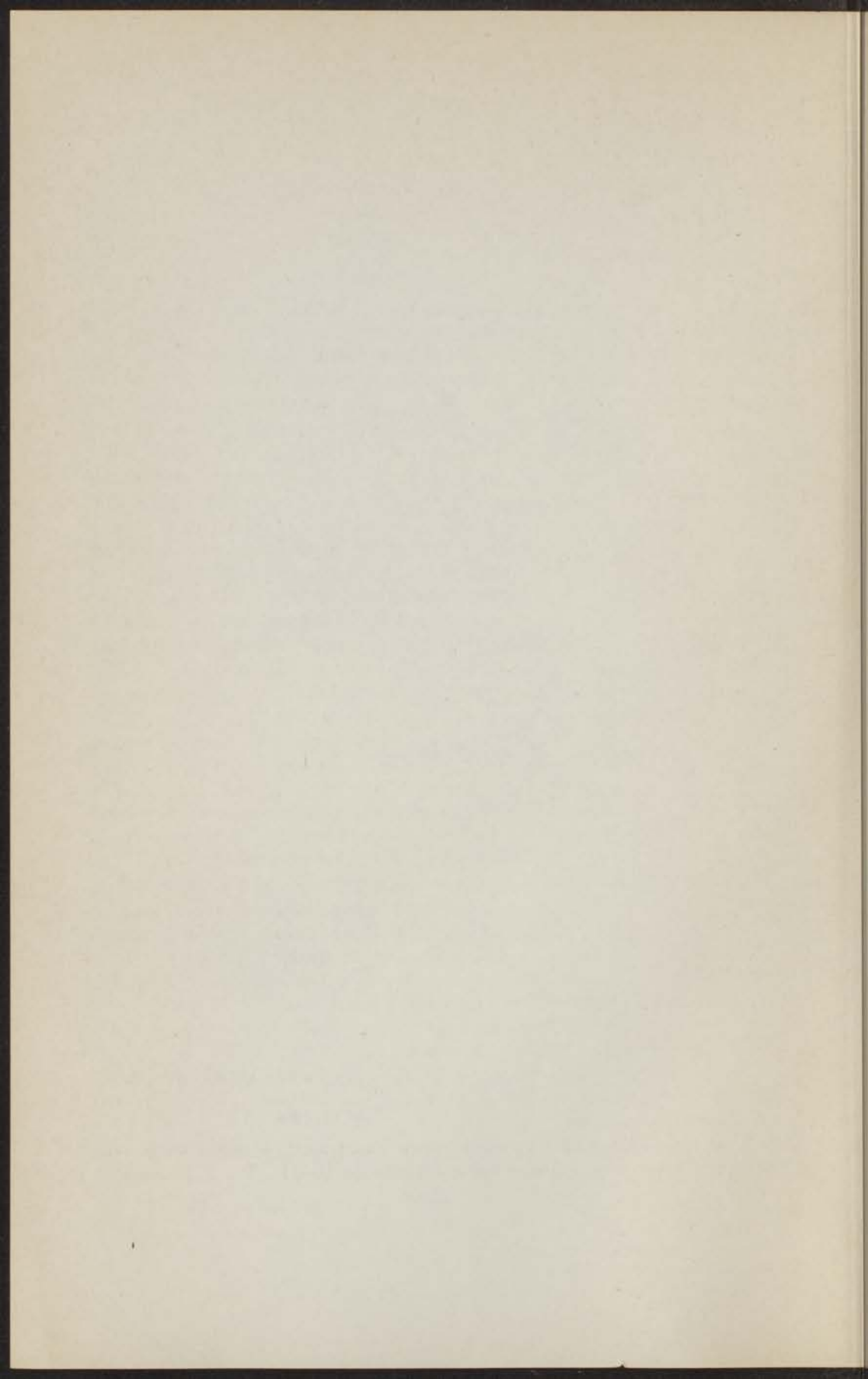
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INTRODUCTION

The first chapter is devoted to a general introduction to the subject of the book. It discusses the importance of the study and the scope of the work. The second chapter deals with the theory of the subject. It discusses the various aspects of the theory and the methods used in the study. The third chapter is devoted to the experimental work. It describes the apparatus used and the results obtained. The fourth chapter discusses the results of the study and compares them with the theoretical predictions. The fifth chapter is a summary of the work and a discussion of the conclusions drawn from the study.

AAN MIJN OUDERS
AAN MIJN VROUW



INTRODUCTION

Liquid ${}^4_2\text{He}$ displays a number of remarkable properties which are presumably due to exceptionally large quantum effects. As the most fundamental property we mention that two different states of the liquid exist which pass into each other at a certain temperature, called the lambda-temperature. The latter is 2.186°K at the pressure of the saturated vapour and decreases slightly when the pressure is raised. Above this temperature the liquid, called He I, behaves in many respects like other liquids, but below 2.186°K the behaviour of liquid helium, called He II, is quite anomalous. Some peculiar phenomena which can be observed in He II are the following:

A solid surface in contact with the liquid is covered with a very thick, mobile, film. Under the influence of gravity or of a temperature gradient this film will 'creep' along the surface, reaching velocities which are of the order of 20 cm/sec .

The flow of the liquid through a capillary, or a narrow slit, is governed by the temperature gradient along the capillary as well as by the gradient of the pressure. In the case that the temperature gradient is given, the flow of the liquid will tend to be such as to cause a pressure gradient proportional to the gradient of the temperature and having the same sense as the latter. This phenomenon is called the fountain effect. The inverse effect, called mechano caloric effect, has also been observed.

The heat conductivity of the bulk liquid is anomalously large. This explains, for instance, the well-known fact that He II cannot be made to boil. No temperature difference can be maintained between the inside of the liquid and the surface.

Temperature waves can be propagated without appreciable attenuation. This phenomenon is called second sound as distinguished from ordinary, or first, sound. Second sound waves are not accompanied by variations of the density.

The internal friction of He II appears to be associated only with a certain part of the liquid, as can be demonstrated by the following experiment:

A set of parallel horizontal vanes suspended by means of a fine torsion thread are allowed to oscillate in He II. The gaps between

the vanes and the frequency of oscillation are both so small that normally one would have expected all the liquid in the gaps to cling to the vanes. When, however, the mass of the oscillating liquid is computed from the period of the oscillations, it is found that only part of the liquid clings to the vanes. The remaining part seems to have no detectable viscosity.

The above phenomena can be described in terms of a two fluid model, as suggested by Tisza¹⁾. According to this model helium II can be formally divided into two interpenetrating fluids, which possess separate velocity fields. One of these fluids has practically no viscosity and is therefore called the 'superfluid' while the other has a viscosity of about the same magnitude as that for He I and is called the 'normal fluid'; the concentration of the fluids is a function of the temperature. At zero temperature helium II is pure superfluid but the concentration of the latter falls with temperature and at the lambda-point no superfluid is left.

Landau²⁾ has proposed another theory. He suggests that two elementary types of motion of the liquid may be distinguished which he calls 'phonons' and 'rotons'. Phonons are taken to be quanta of longitudinal compressional waves, i.e. sound waves, but the nature of the rotons is not well understood. The above theories have to a large extent a phenomenological character. Recently, however, attempts have been made to construct a theory of He II on a more fundamental basis.^{3) 4)}

In one of these recent theories³⁾ the idea that the λ transition in liquid helium can be regarded as a Bose - Einstein condensation phenomenon has been re-examined from the point of view that the interaction of the particles in the liquid is strong. This leads to a confirmation of the results obtained by London in an earlier treatment⁵⁾, which was based on the assumption that liquid helium may to a first approximation be treated as an ideal gas.

In the present thesis two investigations are described which may shed some light on certain aspects of the helium problem. In the first one the transport of momentum in the liquid is studied in the temperature region above the transition point, so in helium I. In the second one the adsorption of the vapour on a solid surface is investigated at temperatures below 2.186 °K.

In chapter I we have discussed some theories of momentum transfer, whereas in chapter II a description is given of an experimental determination of the viscosity of helium I at higher densities. In the end section of chapter II we have discussed the significance

of the experimental data, in particular of those which correspond with temperatures in the immediate neighbourhood of the λ -transition. In the first section of chapter III we have considered some theories regarding multilayer adsorption, whereas in the second section a description is given of an experimental investigation on the adsorption of helium gas at relative pressures close to saturation and at temperatures below the λ -temperature. The experimental results have been discussed in the final section of chapter III.

CHAPTER I

VISCOSITY OF DENSE FLUIDS.

1. *Transfer of momentum.* The definition of the viscosity of a fluid can be obtained from a consideration of a fluid layer, infinite in extent, in which exist the macroscopic velocities $u = z \, du/dz$, $v = 0$, $w = 0$ in the x , y and z direction, du/dz being a uniform velocity gradient.

The viscosity is then equal to the transport of the x component of momentum in the z direction per unit time, per unit surface area and per unit velocity gradient.

In gases of low densities the transport of momentum is due to diffusion, since a molecule carries momentum with itself when moving through empty space between collisions. At higher densities, on the other hand, the momentum transport is to a large extent due to the forces between the molecules. In the following we shall suppose that the molecules are spherically symmetrical and that the action of the intermolecular forces is confined to nearest neighbours. We shall distinguish between two types of molecular interaction. Let r be the distance between two given molecules M_1 and M_2 , a the average molecular distance and σ the minimum distance. According to our assumptions there exists a certain distance $r = \sigma + \Delta\sigma$ beyond which the forces between M_1 and M_2 may be ignored. The first type of interaction then occurs when $\Delta\sigma$ is small in comparison with $a - \sigma$, whereas the second type of interaction occurs when $\Delta\sigma$ is of the same order as $a - \sigma$.

When the interaction is of the first type, a given molecule may for most of the time be regarded as a free particle and the interaction between two, or more, molecules at a given moment can be considered as a collision which is characterized by the respective initial and final velocities. The transfer of momentum is caused by the following processes:

- a. Molecule centres, such as M_0 , pass the xy plane (see fig. 1), in which case the momentum carried by them is transferred in the z direction.
- b. Momentum is exchanged at binary and multiple collisions, which are such that one part of the molecule centres is situated in the upper halfspace whereas the other part is in the lower halfspace.

In fig. 1 we have represented a binary collision; the centre of the molecule M_2 lies on the sphere of closest approach around M_1 .

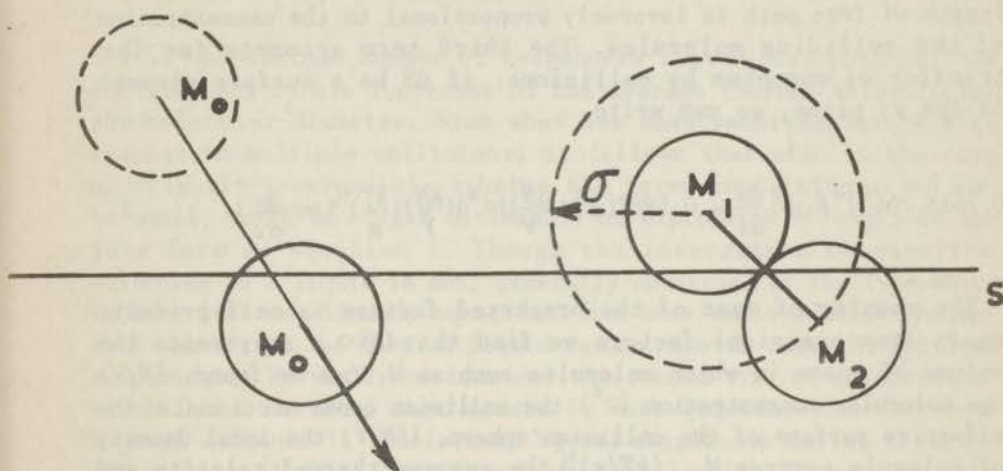


Fig. 1 Transfer of momentum

At high densities, where the free path of the molecules is of the same order as the diameter σ , the transfer of momentum is mainly due to collisions. When a dense gas consists of rigid elastic spheres the number of multiple collisions may be ignored against the number of binary collisions and the following expression can be derived for the viscosity (Enskog).

$$\eta = \eta_0 \left\{ 1/K + 0.8000 b/V + 0.7614 (b/V)^2 K \right\} \quad 1$$

$$\text{where } \eta_0 = 5/16 \sigma^2 (mkT/\pi)^{1/2} \quad 2$$

is the viscosity of the gas of low density,

$b = 2/3 \pi N \sigma^3$ is the excluded volume of the molecules,

V is the volume of the gas and

K is the ratio between the local density of molecule centres M_2 at the surface of the collision sphere of a given molecule M_1 and the average density N/V . K is equal to unity at low densities of the gas and increases when the density increases.

An analysis of the derivation of eq. 1 shows that each of the

three terms of the right hand member has an independent physical meaning. The first term, τ_0/K , gives the transfer of momentum by diffusion which also takes place in the gas of low density. The factor $1/K$ which appears here takes account of the fact that the length of free path is inversely proportional to the concentration of the colliding molecules. The third term accounts for the transfer of momentum by collisions; if dS be a surface element of the xy plane, we can write

$$0,7614 \tau_0 \left(\frac{b}{V}\right)^2 K dS \frac{du}{dz} = 0.5887 (dS\sigma) \left(\frac{N}{V}\right) (\sigma^2) \left(\frac{KN}{V}\right) \left(\frac{kT}{m}\right)^{1/2} (m\sigma \frac{du}{dz}) \quad 3$$

The meaning of most of the bracketed factors is self-evident; apart from numerical factors we find that $(dS\sigma)$ represents the volume of space in which molecules such as M_1 can be found, (N/V) the molecular concentration (σ^2) the collision cross section i.e. the effective surface of the collision sphere, (KN/V) the local density of molecule centres M_2 , $(kT/m)^{1/2}$ the average thermal velocity and $(m\sigma du/dz)$ the difference in momentum of flow between colliding molecules.

The second term in (1) arises from the fact that the molecules, at the moment of collision, have travelled a certain mean free path, with the result that the difference in flow velocity between them is actually larger than would follow from the position of their centres. The extra difference is proportional to the average free path, hence inversely proportional to KN/V which means that the second term depends on the average density only.

When the assumption that the molecules are impenetrable spheres is dropped, we can no longer ignore the number of multiple collisions in comparison with the number of binary collisions. As a first approximation, however, a ternary collision can be regarded as two coinciding binary collisions, so that the former has to be taken into account only when the average result of such a collision, differs from the average result of two binary collisions. An analogous argument may be applied to the other multiple collisions (van Wyk and Seeder^{*}). The probability of a multiple collision between a given molecule M_1 and j neighbours M_2 will be proportional to $(KN/V)^j$ so that we obtain an equation of the following character for the viscosity of a gas consisting of slightly compressible spheres:

^{*}) Van Wijk, W.R. and Seeder, W.A. *Physica* 4 (1937) 1073

$$\eta = \sum_{j=-1}^{\gamma} c_j (N/V)^{j+1} K^j$$

γ is the maximum number of neighbours that M_1 can possess; the coefficients c_j are functions of the average thermal velocity and the molecular diameter. From what has been remarked before with respect to multiple collisions, it follows that also in the case of slightly compressible spheres the terms containing $j > 3$ may be small, hence we obtain ultimately an expression which is of the same form as equation 1. Though the interaction between the molecules in a liquid is not, generally speaking, of the type which we have just considered, equation 1 has been employed with remarkable success in the case of liquid carbon dioxide near the critical temperature. We shall now consider the second type of interaction, which is of the kind that occurs in most liquids. When $\Delta\sigma = a - \sigma$ a given molecule is accelerated by its neighbours during most, or all, of the time, so we can no longer distinguish between separate collisions. Owing to the latter circumstance, the mathematical treatment of the above case becomes very complicated. There may, however, be perceived some analogy between the motion of a molecule of a dense fluid which gradually pushes away, as it were, the surrounding molecules and the Brownian motion of a small solid sphere in a viscous fluid⁶⁾. We can then assume that the interaction between a given molecule M and the neighbouring molecules may, in the case that the liquid is in equilibrium, be characterized by a friction constant ζ (as in the case of Brownian motion), which depends on the nature of the liquid as well as on the temperature and the density of the latter. The friction constant ζ of the Brownian motion can be computed from the self-diffusion constant D of the fluid, according to Einstein's relation

$$D = kT/\zeta$$

We see therefore that the relation between the viscosity, which we can expect to be directly proportional to ζ , and the diffusion constant is quite different from that which is found in the case of a dilute gas.

Till now we have supposed that the viscosity of the fluid is entirely due to the forces between the molecules, represented by the coefficient ζ . In reality the transfer of momentum by diffusion

of the molecules must also be taken into account. We may write therefore

$$\eta = \eta' + \eta'' \quad 3$$

where η' represents the transfer of momentum by diffusion, which is directly proportional to the self-diffusion coefficient D , whereas η'' represents the transfer of momentum by the intermolecular forces.

Attempts to establish a rigorous theory of transport phenomena in liquids have been made by Born and Green⁷⁾ and by Kirkwood⁸⁾.

The part of the viscous force which is due to the molecular interaction is now interpreted as the tangential component of the average force exerted by the molecules M_2 in the upper halfspace on the molecules M_1 in the lower halfspace across a surface element dS of the xy plane (see fig. 1). (The forces between a pair of molecules may be said to 'act across dS ' when the line joining the centres, r_{12} , is intersected by the surface element.) The partial viscous force is then given by the following expression

$$\eta'' \frac{du}{dz} dS = 1/2 (N/V)^2 dS \iiint \frac{z_{12} x_{12}}{r_{12}} \frac{\partial \epsilon}{\partial r_{12}} g(x_{12}, y_{12}, z_{12}) dx_{12} dy_{12} dz_{12}$$

where $\epsilon(r_{12})$ denotes the potential energy of a pair of molecules and $g(x_{12}, y_{12}, z_{12})$ the ratio between the local density and the average density in the fluid. The value of the integral differs from zero because $g(r)$ is no longer spherically symmetrical, as would be the case when the fluid is in equilibrium. The amount of distortion of $g(r)$ is proportional to the gradient of the flow and inversely proportional to the friction constant ζ . In the case of short range forces, which we are considering here, only the first maximum of the local distribution function $g(r)$ contributes appreciably to the value of the integral, so to η'' .

The value of η' can be computed when the velocity distribution of the molecules is known.

Kirkwood has formulated the hypothesis that, for a given liquid, there exists a characteristic time τ , which is such that the forces which act on a molecule at the times t and t' are statistically independent, provided that $t' - t > \tau$. On account of this hypothesis Kirkwood has been able to show that the theory of

Brownian movement actually applies to individual molecules, and to pairs of molecules. With the aid of the latter theory one can derive the probability distributions which are necessary for the calculation of the viscous stress. Kirkwood, Buff and Green⁹⁾ have in this way computed a numerical value for the viscosity of liquid argon, at the normal boiling point. They found 1.27 c.g.s. whereas the experimental value is 2.39 c.g.s.; the agreement may be called reasonable, in view of the large number of approximations which is needed. The empirical data on which the calculation was based, were derived from the X-ray diffraction pattern and from the potential of molecular interaction. In contrast to the case of liquid argon, quantum effects will considerably influence the motion of the atoms in liquid helium, even at temperatures above the λ -point. This is for instance shown by the unusually low density of the liquid which is a consequence of the repulsion of the atoms caused by their large zero-point motion. The quantum theory of transport phenomena in liquids¹⁰⁾ (Born and Green, Eisenschitz, Irving and Zwanzig) is as yet only in an initial stage, however, and for this reason we have made no attempt at an detailed calculation of the viscosity coefficient of He I. Instead we shall confine ourselves to a discussion of the viscosity on the basis of a model, according to which the liquid is treated as an assembly of hard spheres. The diameter, σ , of the spheres can be taken to represent the repulsive forces between the atoms and so will depend on the temperature and perhaps also on the density. Because He I is a simple monoatomic liquid we may assume a simple relation to exist between σ and the specific volume of, for instance, the solidifying liquid. When σ is known, the viscosity of the liquid can be estimated according to eq. 1, provided that the local density factor K , which affects the probability of a collision is given as a function of σ and of the average density.

2. *The local density factor K .* In the case of a gas of hard elastic spheres with given diameter σ , the local density factor can be obtained from the equation of state (Enskog) through the relation,

$$pV/NkT = 1 + bK/V$$

Boltzmann has already derived an approximate expression for the left hand member of 4 in the case of moderate densities, which is the following,

$$pV/NkT = 1 + b/V + 5/8 (b/V)^2 \dots\dots\dots 5$$

The same expression has been obtained by Ursell by means of a more general method which in principle could be so extended as to yield the complete series. In the case of high concentrations however, the necessary computations become extremely difficult and have not actually been carried out. Other approximations have been given by Tonks and by Rice ¹¹). Tonks has based his treatment on the theory of the equation of state of a one-dimensional gas. This theory can be extended to a three-dimensional gas provided that the latter is very dense, because then each molecule may be thought of as being confined to a separate cell, the shape of which can be reasonably defined.

Let us consider a set of N impenetrable molecules, which are confined to a line segment with the length l . The force f exerted by a given particle on each of its neighbours is then equal to

$$f = kT/l_1(1 - \theta) \quad ; \quad 0 \leq \theta \leq 1 \quad 6$$

where $l_1 = l/N$ is the length per molecule and $\theta = N\sigma/l$ is the fraction of the line occupied by the particles. The quantity $l_1(1 - \theta)$ may be regarded as the free length per molecule. In the case of a three-dimensional gas of high density an exact expression for the equation of state might be given if the molecules were arranged in a simple cubical array since in this case the gas might be considered as consisting of linear rows of molecules. The length a per molecule in each row would be equal to $a = (V/N)^{1/3}$ and the free length per molecule would be equal to $a_c(1 - \theta_c^{1/3})$ where θ_c denotes the fractional occupation number so $\theta_c = \sigma^3/a_c^3$. Hence the thrust exerted by a single row on the wall of the vessel containing the gas would be given by the expression

$$f = kT/a_c(1 - \theta_c^{1/3})$$

so, taking into account the number of parallel rows per unit surface, the equation of state becomes

$$pV/NkT = 1/(1 - \theta^{1/3}) \quad 7$$

Actually the configuration of the molecules will be either face-centered cubic or hexagonal in the case of high concentrations. It is probable however that 7 remains a good approximation to the equation of state in this case when the fractional occupation number θ_c is replaced by $\theta = \sigma^3/a^3$ where a again denotes the average distance between the atoms, so

$$a = (\sqrt{2} V/N)^{1/3} .$$

Considering that $b/V = 2.962 \theta$, the Boltzmann approximation can be written in terms of the fractional close packing in the following manner,

$$pV/NkT = 1 + 2.962 \theta + 5.483 \theta^2 + \dots$$

This approximation has been graphically represented by curve a in fig. 2.

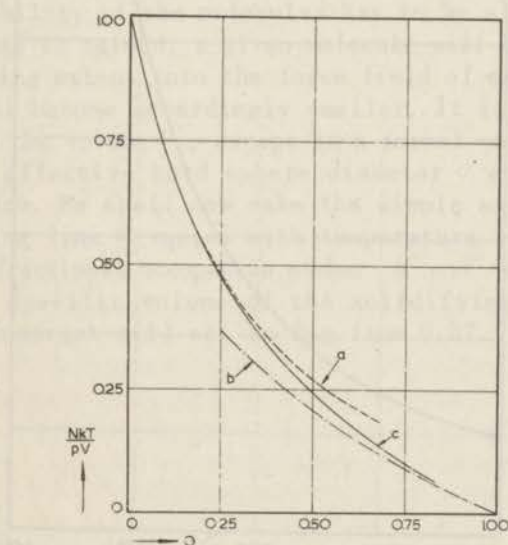


Fig. 2 The equation of state of a gas of hard spheres

Curve a drawn according to eq. 5

Curve b drawn according to eq. 7

Curve c drawn according to eq. 8

By combining the above expression with 7, represented by curve b in fig. 2, the following relation has been obtained by Tonks,

$$\frac{pV}{NkT} = \frac{1 + 2.962 \theta + 5.483 \theta^2}{1 - 0.8517 \theta^3 - 0.1483 \theta^4} \quad 8$$

The above relation, represented by curve c, can be expected to give a reasonable approximation to the equation of state in the whole range of θ . By a combination of the expressions 4 and 8 we may then arrive at the following approximation to the value of the local density factor K ,

$$K = \frac{1 + 1.851 \theta + 0.2875 \theta^2}{1 - 0.8517 \theta^3 - 0.1483 \theta^4} \quad 9$$

In fig. 3 we have plotted K as a function of the fractional occupation number.

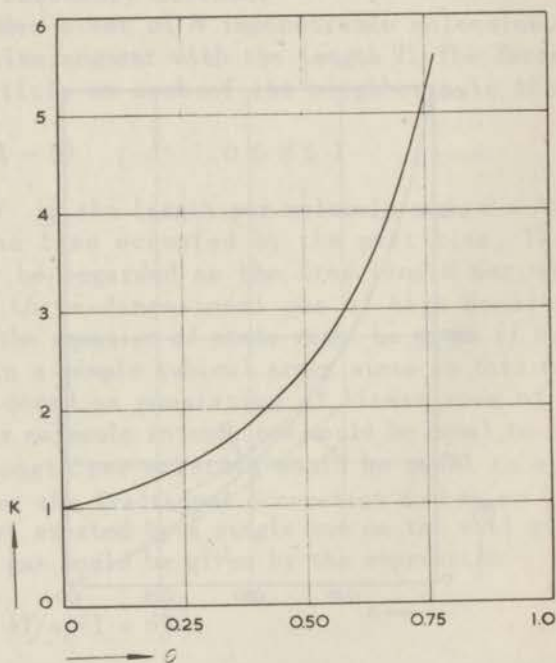


Fig. 3 The local density factor K as a function of the fractional occupation number θ .

3. *Dependence of the molecular arrangement on specific volume and temperature.* When, as a first approximation, the molecules in a body are treated as hard spheres, there is found a smallest volume V' , which corresponds to a close-packed cubic or hexagonal lattice, each particle being in contact with twelve neighbours. With increase of the difference $V - V'$ a gradual increase of disorder in the arrangement of the molecules becomes possible. We must expect, however, that as long as $V - V'$ remains small in comparison with V' , the extra volume cannot be distributed continuously in the body, but only in the form of individual holes, which are of the size of a molecule, so the lattice does not vanish. A breakdown of the crystal lattice can take place only when the number of holes reaches a certain not very small fraction, a few per cent, say, of the number of particles (Kirkwood, Frenkel) ¹²). Thus complete absence of long range order is possible only when the volume is larger than a certain volume V'' . From experiments conducted with glass spheres, Rice concludes that $V'/V'' = 0.87$. V'' will not depend on temperature, as long as the molecules are regarded as rigid spheres, but in reality the compressibility of the molecules has to be allowed for. When the temperature is raised, a given molecule will be able to penetrate to a growing extent into the force field of an adjacent molecule, so V'' will become accordingly smaller. It is no longer possible to define the volume V' , except in a formal way, when we introduce again an effective hard sphere diameter σ which now depends on temperature. We shall now make the simple assumption that along the melting line σ varies with temperature in such a way that a constant fractional occupation number $\theta'' = V'/V''$ can be associated with the specific volume of the solidifying liquid. The value of this constant will not be far from 0.87.

CHAPTER II

INFLUENCE OF PRESSURE ON THE VISCOSITY OF He I

1. *Introduction.* We have already mentioned that the peculiar properties of He II lead us to consider the latter liquid as consisting of two fluids, called normal fluid and superfluid. The fact that the viscosity of the superfluid is zero is particularly intriguing, since at first sight it would seem that the atoms in He II fail to exchange momentum in spite of the fact that the average distance between adjacent atoms is of the same magnitude as their diameter. It seemed to us that some information with respect to the interaction of the atoms might be obtained through an investigation of the transfer of momentum in liquid helium at temperatures where quantum effects are strong without, however, being dominant to such an extent as to prevent a comparison with other liquids. For our purpose the He I region seemed very suitable because experimental evidence seems to indicate that from the boiling point down to about 3°K He I can be regarded as a comparatively normal liquid whereas from 3°K down to the λ -temperature quantum effects become increasingly important. It may further be noted that the variation of the viscosity-coefficient with the temperature appears to be gradual even at the λ -transition, as can be seen from fig. 4. In liquid helium at the pressure of the saturated vapour the zero-point motion of the atoms is large whereas the attractive forces are comparatively weak. The results in a low molecular concentration of the liquid and in connection with the latter circumstance the opinion has sometimes been expressed that the transfer of momentum would be due to the diffusion of the atoms as in the case of a dilute gas. The latter circumstance would then be the cause of the positive value of $d\eta/dT$ in the case of He I. In the present chapter, on the other hand, arguments will be presented to the effect that the momentum transport in He I is in the main caused by the interactions between the atoms, which are, at ordinary pressures, only slightly weaker than in other liquids. In the case of compressed He I we have found that the viscosity varies with the temperature in essentially the same manner as in the case of other liquids,

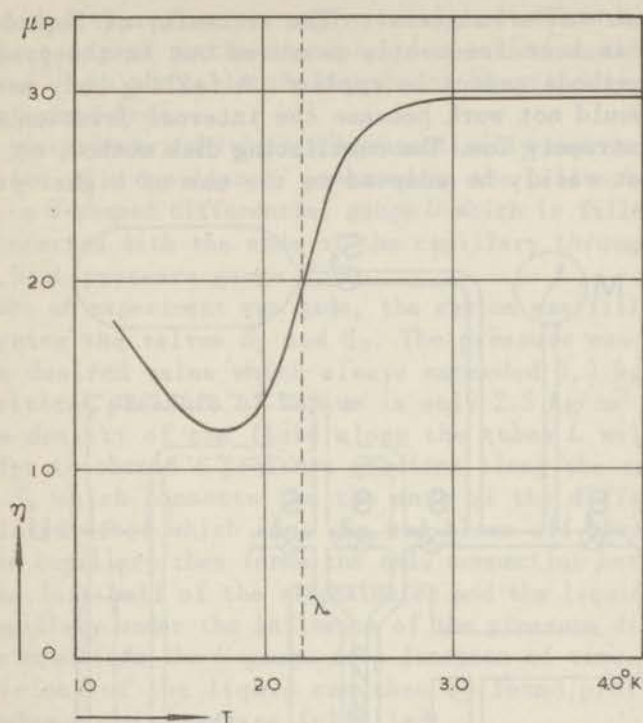


Fig. 4 Variation of the viscosity of liquid helium with temperature ¹³⁾

provided that the temperature is not close to the transition temperature; so the viscosity decreases with increasing temperature. In the case of temperatures and pressures in the neighbourhood of those corresponding with the transition line, on the other hand, we have found that $d\eta/dT$ remains positive even at the highest pressures compatible with the liquid state. In behalf of a comparison between liquid helium and other liquids we have determined a few values of the viscosity coefficient corresponding with temperatures and pressures close to the melting line. Our data appear to be in fair agreement with the values which can be calculated from the atomic mass, the interatomic distance in the liquid and the Debye temperature of solid helium through an equation which has been given by Andrade. ¹⁴⁾

2. *Experimental arrangement.* The viscosity of liquids at high pressures has been frequently measured but in the present case the usual methods cannot be applied. A falling body method, for instance, would not work because the internal friction of liquid helium is extremely low. The oscillating disk method, on the other hand, cannot easily be adapted to the use of higher pressures.

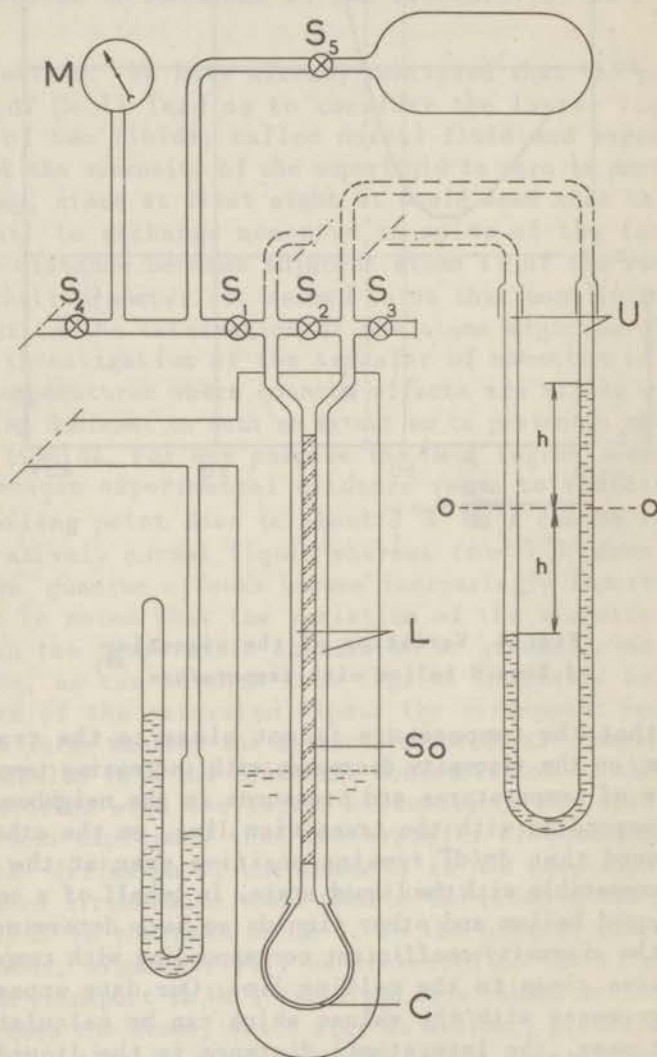


Fig. 5 Viscosimeter

We decided therefore to employ a method which is to a certain extent analogous to the transpiration method used by Michels and Gibson¹⁵⁾ in their determination of the viscosity of nitrogen at high pressures.

The viscosimeter which is diagrammatically represented in fig. 5 consisted of a capillary C immersed in the helium bath inside the Dewar, a U -shaped differential gauge U which is filled with mercury and connected with the ends of the capillary through the lines L , and a high-pressure gauge M .

Before an experiment was made, the system was filled with helium by opening the valves S_1 and S_2 . The pressure was then adjusted to the desired value which always exceeded $3,0 \text{ kg/cm}^2$. Because the critical pressure of helium is only 2.5 kg/cm^2 the variation of the density of the fluid along the tubes L will be gradual. In order to obtain a pressure gradient along the capillary C the valve S_2 which connects the two ends of the differential gauge was closed after which some gas was blown off through the valve S_3 . The capillary then forms the only connection between the right and the left half of the viscosimeter and the liquid flows through the capillary under the influence of the pressure difference which can be read from the U -gauge as a function of time. The viscosity coefficient of the liquid can then be found, provided that the following conditions are fulfilled:

1. The two halves of the viscosimeter must be symmetrical. The tubes L were therefore of identical construction. So as to ensure good thermal contact the tubes were soldered together over their whole length as indicated in fig. 5 by S_0 .
2. The variation of the average pressure in the apparatus during the course of a single run should be small. These variations are caused by the lowering of the bath level and by fluctuations in the temperature of the helium vapour in the Dewar. It can be shown that the influence of the above temperature fluctuations on h , the deviation of the mercury levels from their zero-position $0 - 0$, is directly proportional to the value of h itself, provided that condition 1 is fulfilled.
3. The gas flow through the lines L which occurs during a run should be kept small, because this flow results in the temperature distribution of the gas not being the same as in the case of equilibrium. In order to detect a possible influence of the above effect on our results, runs were made with tubes and capillaries of widely different diameters. The flow velocity was also widely varied. No significant change was

observed in the results of the measurements, however. Moreover it can be shown that actually no correction for the gas flow will be necessary provided that the latter is kept sufficiently small.

4. The flow resistance of the connecting lines L must be small in comparison with the resistance of the capillary C .

We shall now derive some formulae concerning the viscosimeter. We write for the mass of fluid in the system, using the subscripts 1 and 2 for the right and the left half:

$$G_1 = \int \rho(T, p_1) dv_1 - p_1 \pi r^2 h / RT^* ,$$

$$G_2 = \int \rho(T, p_2) dv_2 + p_2 \pi r^2 h / RT^* ,$$

where ρ is the density in g/cm^3 , p is the pressure in $dyne/cm^2$, R is the gas constant in $dyne\ cm/g\ deg.\ K$, T^* is room temperature in $deg.\ K$ and r is the radius of the U -tube.

The integration is performed over the volume in T and in U , including the volume in each leg up to $0 - 0$. In this notation we have taken into account that the density ρ is a single-valued function of the temperature and pressure if either one or the other exceeds its critical value. We define the mean pressure $p = \frac{1}{2}(p_1 + p_2)$ and shall use the subscript 0 when the deviation h is zero. In order to find the variation in the mean pressure associated with h , we write, assuming a stationary temperature distribution:

$$G_1 = \int \rho(T, p_0) dv_1 + [p - h/a - p_0] (\partial/\partial p_0) \int \rho(T, p_0) dv_1 - (p - h/a) \pi r^2 h / RT^*$$

$$G_2 = \int \rho(T, p_0) dv_2 + [p + h/a - p_0] (\partial/\partial p_0) \int \rho(T, p_0) dv_2 + (p + h/a) \pi r^2 h / RT^*$$

where $1/a = \rho_{mercury}^* g$, g being the gravity acceleration and the asterisk denoting room temperature:

Introducing

$$G_{10} = \int \rho(T, p_0) dv_1 \quad G_{20} = \int \rho(T, p_0) dv_2$$

and observing that $G_1 + G_2 = G_{10} + G_{20}$, because the total mass does not depend on h , and that $\partial G_{10}/\partial p_0 = \partial G_{20}/\partial p_0$ which we shall abbreviate to $\partial G_0/\partial p_0$ we obtain:

$$p = p_0 - \pi r^2 h^2 / (aRT^* \partial G_0/\partial p_0)$$

so:

$$G_1 = G_{10} - \frac{h}{a} \frac{\partial G_0}{\partial p_0} - p_0 \frac{\pi r^2 h}{RT^*} + \frac{\pi^2 r^4 h^3}{aR^2 T^{*2} \partial G_0/\partial p_0} \quad 10$$

One obtains for the flow, by differentiating (10) with respect to time:

$$\frac{dG_1}{dt} = - \left[\frac{p_0 \pi r^2}{RT^*} + \frac{\partial G_0/\partial p_0}{a} - \frac{3\pi^2 r^4 h^2}{aR^2 T^{*2} \partial G_0/\partial p_0} \right] \frac{dh}{dt}$$

hence, for laminar flow,

$$- \frac{\rho_{liquid} \pi s^4 2h}{8\eta L a} = \left[\frac{p_0 \pi r^2}{RT^*} + \frac{\partial G_0/\partial p_0}{a} \right] \frac{dh}{dt} \quad 11$$

where s is the radius of the capillary C , L its length, and η the viscosity coefficient of the liquid.

Deriving (11) we have neglected the difference in hydrostatic pressure of the gas, the flow resistance of T and in the right hand member the term $3\pi^2 r^4 h^2 [aR^2 T^{*2} \partial G_0/\partial p_0]^{-1}$ which is about one thousandth of the two remaining terms. The deviation h is given by:

$$\log h = \log h_1 - \frac{t - t_1}{\eta} \frac{\rho_{liquid}}{\rho_{gas}^*} \left[\pi r^2 + \frac{RT^*}{p_0 a} \frac{\partial G_0}{\partial p_0} \right]^{-1} \frac{2\pi s^4 \log e}{8L}$$

11bis

where h_1 and t_1 are integration constants and $\rho_{gas}^* = p_0/RT^*$ is the density of the gas in the U -gauge.

In this derivation it is assumed that the temperature distribution

remains stationary; actually, however, it varies systematically owing to

1°. the lowering of the bath level

2°. the variation of the gas flow in the connecting tubes L .

When equation (10) is varied with the condition that G_1 is constant, we find for a slight deviation of the temperature distribution the following expressions:

$$0 = \int \frac{\partial \rho}{\partial T} \delta T_1 dv_1 - \delta h \left[\frac{1}{a} \frac{\partial G_0}{\partial p_0} + \frac{p_0 \pi r^2}{RT^*} \right] + \delta p_0 \left[\frac{\partial G_0}{\partial p_0} - \frac{\pi r^2 h}{RT^*} \right] \quad 12$$

$$0 = \int \frac{\partial \rho}{\partial T} \delta T_2 dv_2 + \delta h \left[\frac{1}{a} \frac{\partial G_0}{\partial p_0} + \frac{p_0 \pi r^2}{RT^*} \right] + \delta p_0 \left[\frac{\partial G_0}{\partial p_0} + \frac{\pi r^2 h}{RT^*} \right]$$

Ad 1°. In this case is $\delta T_1 = \delta T_2$ and we obtain from the above equations:

$$\delta h_1 = -\delta p_0 \pi r^2 h \left[(RT^*/a) \frac{\partial G_0}{\partial p_0} + p_0 \pi r^2 \right]^{-1} \quad 13$$

The correction δh_1 for the lowering of the bath level can thus easily be found from the corresponding change in the equilibrium pressure δp_0 .

The connection between the latter and the variation of the temperature distribution is given by the expression:

$$\delta p_0 = \frac{\int (\partial \rho / \partial T) \delta T dv}{(\partial G_0 / \partial p_0)} \quad 14$$

Ad 2°. As a result of the gas flow the average temperature in a given cross section of a connecting tube will differ from its equilibrium value and to a first approximation is: $T'_1 = T_1 + \delta T_{12}$, $T'_2 = T_2 + \delta T_2$; $\delta T_1 = -\delta T_2$ for the gas, while at the wall $T'_1 = T_1 = T'_2 = T_2$. From the equations (12) it follows that now: $\delta p_0 = 0$, thus we obtain the following correction δh_2 ,

$$\delta h_2 = [RT^* \int (\partial \rho / \partial T) \delta T dv] \cdot [(RT^*/a) (\partial G_0 / \partial p_0) + p_0 \pi r^2]^{-1} \quad 15$$

If there were no heat flow to the wall, the variation with time of the temperature in a cross section would be: $\partial T/\partial t = w \partial T/\partial x$, where w is the velocity of the gas and x is the distance along the tube. This corresponds with a heat source along the axis $H = \pi \sigma^2 w \rho c_p \partial T/\partial x$ where σ is the radius of the tube and c_p the specific heat of the gas. Actually H is compensated by the conduction to the wall. When we assume that the time necessary for the latter process to attain a steady state is small compared to the time constant of the U -gauge, the resulting temperature difference δT will be proportional to H and therefore to w , or $\delta h = fh$ from (11) and (15); f is a proportionality factor not dependent on h . So $h' = (1 + f)h$, which shows that the $\log h$, t -curve is displaced parallel to itself. Consequently no correction for the gasflow is required. The situation in a connecting tube may approximately be represented by a cylindrical ring of helium with the outer surface (radius σ) at the temperature T and the inner surface (radius $\sigma/2^{1/2}$) at the temperature $T' = T + \delta T$. The coefficient of heat conductivity is λ . A heat current H is flowing radially through the ring. The temperature distribution along the tube is approximated by taking $\partial T/\partial x = \text{constant}$. We then find, for $\sigma = 0.035$ cm, $\lambda = 6 \cdot 10^{-5}$ cal/deg cm sec, $c_p = 0.5$ cal/g deg, $\rho = 0.15$ g/cm, considering the heat capacity and thermal resistance of the ring, that the time in which the heat conduction to the wall becomes stationary is of the order of a few seconds. The time constant of the U -gauge was, as found experimentally, about four minutes and consequently the assumption, mentioned before, seems to be justified. Estimating δT for a run at $p = 5$ kg/cm² and a temperature of the helium bath $T = 4$ °K we obtain $\delta T = 0.02$ °K. The variation δh is then approximately $\delta h = 0,01 h$.

3. *Experiments and results.* In order to check the accuracy of our method we have repeated the determination of certain values of the viscosity coefficient several times. In fig. 6 $\log h$ is represented as a function of the time $t - t_i$ for a temperature $T = 4.07$ °K and for pressures of 10, 20 and 30 kg/cm². The correction term $RT^* \partial G_0/\partial \gamma_0$ was determined in the following manner:

The calibrated volume V_{cal} of the high-pressure gauge M completed with a section of the attached connecting line were filled with gas up to a pressure p' whereas the pressure in the viscosimeter had the slightly different value p'' . When the valve S_1 was opened

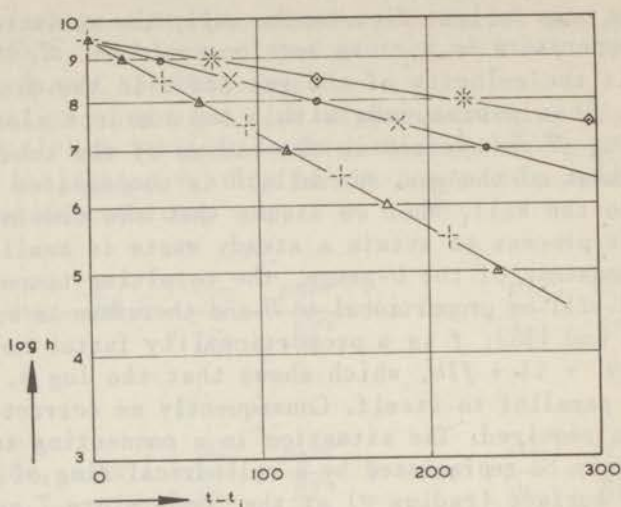


Fig. 6

△	p = 10.5 kg/cm ²	run on 5-4-'51
⊕	p = 9.8 kg/cm ²	run on 25-4-'51
○	p = 19.5 kg/cm ²	run on 5-4-'51
×	p = 19.8 kg/cm ²	run on 25-4-'51
◇	p = 29.8 kg/cm ²	run on 5-4-'51
*	p = 30.0 kg/cm ²	run on 6-6-'51

the pressures in the gauge and in the viscosimeter became equal to p''' , (the valve S_2 remained open during the determination). The following relation then exists between p' , p'' and p''' ,

$$\frac{(p' - p''')}{RT^*} V_{cal.} = 2 \frac{\partial G_0}{\partial p} (p''' - p'')$$

The values of $2RT^* \partial G_0 / \partial p_0$ thus obtained have been plotted as a function of pressure in fig. 7. The uncertainty of the determination is about ten percent which is not serious because $RT^* \partial G_0 / \partial p_0$ is only a correction. We did not find any dependence on the temperature of the bath; this is to be expected because only those parts of the fluid are of importance for the value of the correction term

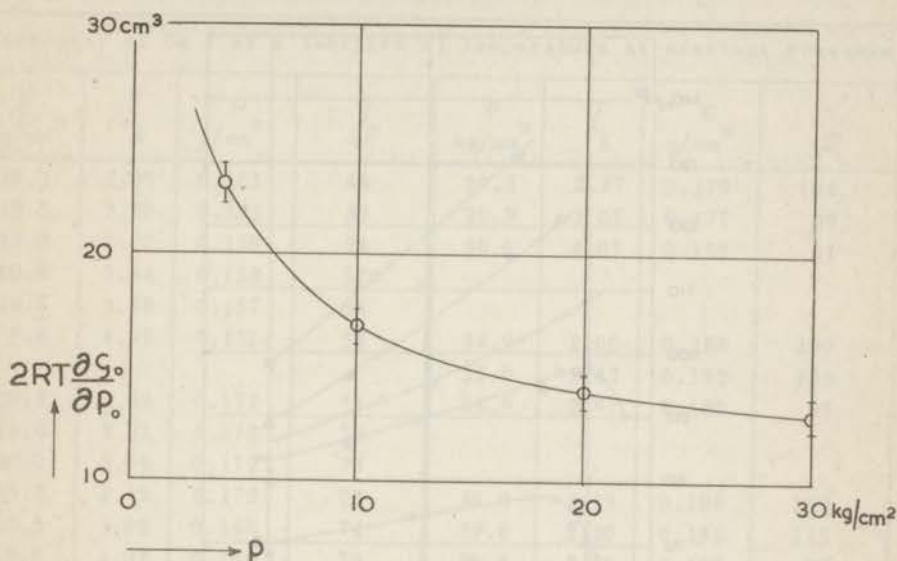


Fig. 7 $2RT^* \frac{\partial G_0}{\partial p_0}$ as a function of p

where the temperature is in the neighbourhood of the critical temperature. The dependence on the pressure, on the other hand, is very marked as can be seen from fig. 7. The rapid increase of the correction term which occurs at lower pressures can be easily understood if one considers that in those parts of the fluid where the temperature is in the neighbourhood of the critical temperature, high values of $\partial \rho / \partial p_0$ occur when the pressure approaches the critical pressure; the latter values give an appreciable contribution to the correction term, which can be written as:

$$RT^* \int \partial \rho / \partial p_0 (T, r_0) dv$$

In order to calibrate the capillary C we made some runs at the normal boiling point of liquid oxygen. The pressure of the gas was 10.0 kg/cm². The viscosity of liquid helium was then obtained

from the ratio η/η_{cal} , where $\eta_{cal} = 91.0 \mu P$. The results have been assembled in table I and figs. 8 and 9.

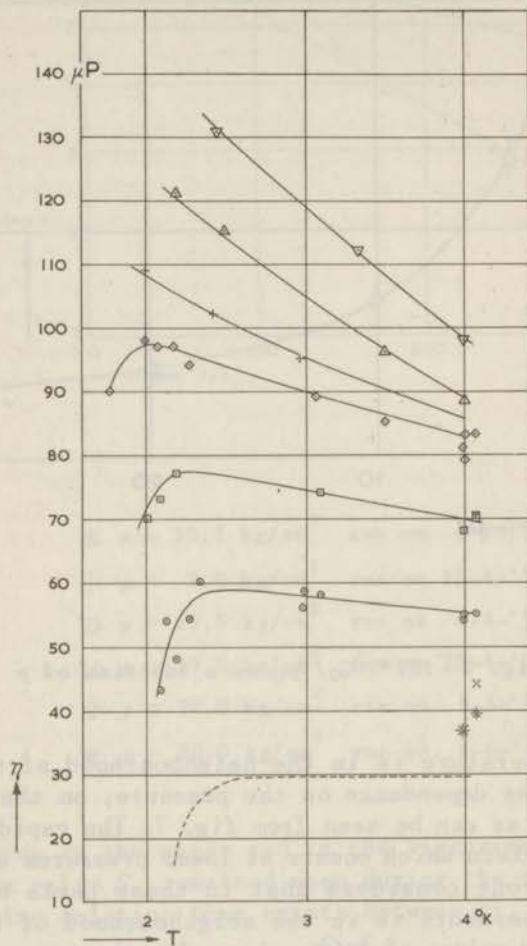


Fig. 8 The viscosity of liquid helium I as a function of the temperature at constant pressure.

∇ $p = 50 \text{ kgcm}^{-2}$ $+$ $p = 35 \text{ kgcm}^{-2}$ \square $p = 20 \text{ kgcm}^{-2}$
 Δ $p = 40 \text{ kgcm}^{-2}$ \diamond $p = 30 \text{ kgcm}^{-2}$ \circ $p = 10 \text{ kgcm}^{-2}$

----- Drawn according to the measurements of Bowers and Mendelssohn, and of De Troyer, Van Itterbeek and Van den Berg¹³⁾.

TABLE I

Viscosity of He I as a function of temperature at constant pressure							
p kg/cm ²	T °K	ρ g/cm ³	η μP	p kg/cm ²	T °K	ρ g/cm ³	η μP
10.2	2.09	0.161	44	29.8	2.27	0.179	94
10.5	2.19	0.161	48	29.9	3.07	0.177	89
10.0	2.27	0.159	54	30.0	4.07	0.172	81
10.0	2.94	0.158	57				
10.5	3.08	0.157	58				
9.8	4.07	0.151	55	34.9	2.00	0.183	109
				35.0	2.43	0.182	103
20.2	1.89	0.172	*)	34.9	2.97	0.180	95
20.0	2.01	0.172	70				
20.0	2.09	0.172	73				
19.8	2.19	0.172	77	40.0	2.19	0.186	122
19.8	3.08	0.168	74	39.8	2.50	0.185	115
19.8	4.07	0.164	70	39.8	3.50	0.183	96
19.9	4.07	0.164	70	39.6	4.03	0.181	88
30.0	1.78	0.179	90				
30.0	2.00	0.179	98	50.0	2.45	0.191	131
30.0	2.09	0.179	97	50.0	3.33	0.189	112
30.0	2.19	0.179	97	50.0	4.03	0.187	98

*) No definite value can be given owing to the anomalous behaviour of the flow.

The Reynolds number never exceeded a value of about 45 in our experiments, from which it can be concluded that the flow was laminar in all cases. The capillary used in most experiments had an effective radius of 5.8μ , which is so small compared with the radius of a connecting tube (0.03 cm) that the flow resistance of the latter can be ignored. So as to check the fulfillment of the first condition (see page 21) the position of the mercury levels was observed for some time after the valve S_2 had been closed, before applying a pressure difference. The fulfillment of the second condition was checked by observing the

pressure in the viscosimeter, during a time which was equal to that needed for a single run. In most cases the pressure variation caused by the lowering of the bath level was found to be less than 0.07 kg/cm^2 which causes only a negligible correction.

4. *Discussion.* With regard to the viscosity of mono-atomic liquids at the melting point Andrade¹⁴⁾ has proposed the following formula

$$\eta = \frac{4}{3} \frac{\nu m}{a}$$

In this expression is ν a frequency characteristic for the molecular motion in the liquid, m the molecular mass and a the average intermolecular distance. When it is assumed that the frequency ν is approximately the same in the liquid as in the solid at the melting point, we can write $\nu = (k/h)\theta_D$ where θ_D is Debye's characteristic temperature. The relation is then found to apply in the case of several liquids, having viscosities of widely varying magnitude. In the case of helium at pressures and temperatures in the neighbourhood of the melting line, the agreement is good, as can be seen from Table II.

TABLE II

Viscosity of He I in the neighbourhood of the melting line					
p kg/cm^2	T $^{\circ}\text{K}$	T_m $^{\circ}\text{K}$	θ_D $^{\circ}\text{K}$	$\eta_{calc.}$ μP	$\eta_{exp.}$ μP
35	2.00	1.88	23	115	109
40	2.19	2.08	24	120	114
50	2.45	2.34	25	128	131

The values of θ_D have been obtained by slightly extrapolating the data given by W.H. Keesom and A.P. Keesom¹⁵⁾, which are in good agreement with those obtained by Simon¹⁶⁾ et.al. We may conclude therefore, that at the pressures and temperatures considered above, helium behaves like a normal liquid. So as to obtain a rough picture of the transfer of momentum in He I we shall discuss our experimental data on the basis of a hard sphere model, as considered in Ch. I. It will be supposed that the effective diameter of the atoms does not depend on the density of the liquid and that the fractional close packing corresponding with the solidifying liquid is constant along the melting line. Good agreement between the experimental values of the viscosity and those yielded by the model can be obtained if we choose $\theta'' = 0.735$, which is not far from $\theta'' = 0.87$. The estimated values have been tabulated along with the experimental values in Table III, whereas in fig. we have plotted the experimental values divided by the corresponding quantity η_0 . The full line represents the quantity η/η_0 according to eq. 1.

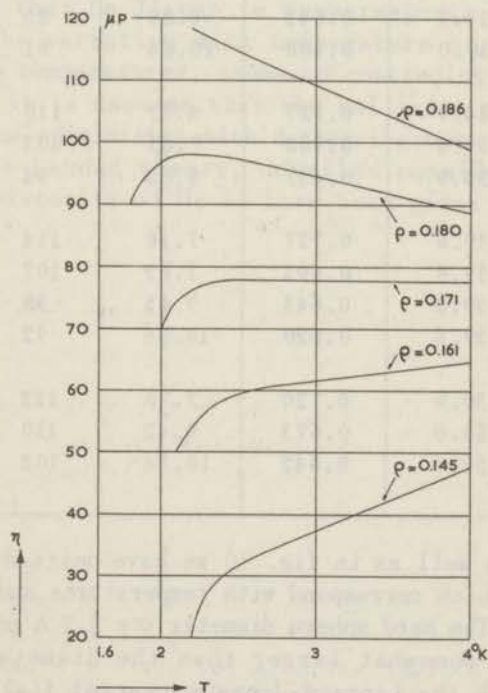


Fig. 9 The viscosity of liquid helium I as a function of the temperature at constant density.

TABLE III

Viscosity of He I as a function of temperature and pressure					
T °K	p kg/cm ²	θ	η_0 μP	$\eta_{est.}$ μP	$\eta_{exp.}$ μP
4.00	0.83	0.434	10.60	43	30
3.08	10.5	0.770	8.95	64	58
4.07	9.8	0.726	10.64	59	55
3.08	19.8	0.600	8.95	77	74
4.07	19.9	0.549	10.64	74	70
2.27	29.8	0.692	7.35	95	94
3.07	29.9	0.641	8.89	85	89
4.07	30.0	0.588	10.64	81	81
2.00	34.9	0.727	6.77	110	109
2.43	35.0	0.700	7.65	103	103
2.97	34.9	0.657	8.83	94	95
2.19	39.8	0.727	7.18	114	114
2.50	39.8	0.691	7.82	107	107
3.50	39.8	0.645	9.65	98	98
4.03	39.6	0.620	10.56	92	92
2.45	50.0	0.720	7.70	122	131
3.33	50.0	0.673	9.42	110	112
4.03	50.0	0.642	10.54	102	98

In table III as well as in fig. 10 we have omitted those values of the viscosity which correspond with temperatures and pressures close to the λ -line. The hard sphere diameter $\sigma = 3.2$ Å corresponding with $\theta'' = 0.735$ is somewhat larger than the diameter which can be associated with the Lennard-Jones potential field of two interacting helium atoms, $\sigma_{L-J} = 2.6$ Å. So as to estimate the relative importance of the diffusion and of the intermolecular

forces we put, $\eta' = \eta_0/K$. and $\eta'' = \eta_0 [4/5 b/V + 0.7614 (b/V)^2 K]$. It is then found that in the neighbourhood of the melting line $\eta' = 0.02 \eta$ whereas $\eta'' = 0.98 \eta$. At ordinary pressures we find $\eta' = 0.15 \eta$ and $\eta'' = 0.85 \eta$ so we are led to the conclusion that even in this case, in spite of the low density of the liquid the viscosity is mainly due to the intermolecular forces. This means that the decrease of the viscosity at temperatures close to the λ -temperature with decreasing temperature cannot be ascribed to the variation of the molecular velocity, but that it must sooner be interpreted as a decrease of the collision probability when we speak in terms of the hard sphere model.

In the case of He II we seem to encounter a somewhat similar phenomenon with respect to the collisions of the excited molecules which constitute the 'normal fluid'. Experimental evidence, such as the low density of the 'normal fluid', the large diffusion coefficient of ^4He in He II (Taconis c.s.)¹⁷⁾ and the Knudsen effects¹⁸⁾ which occur when He II flows through very narrow slits, suggests that He II can in many respects be treated as a dilute gas. The variation with temperature of the viscosity of He II, at low temperatures, seems to contradict this picture, however, unless it is assumed that the collision probability of the 'excited atoms' diminishes with decreasing temperature. Within the frame of the Landau theory, detailed considerations with respect to the viscosity of He II have been given by Landau and Khalatnikov¹⁹⁾.

CHAPTER III

ADSORPTION OF HELIUM ON GLASS AT TEMPERATURES BELOW THE λ -POINT

1. *Introduction.* In 1936 it was discovered that a thick film is formed on a solid surface, which is in contact with liquid helium II or with its vapour (Rollin, Kikoin and Lasarev²⁰), which film shows very remarkable transport properties (Daunt, Mendelssohn²¹). Estimates of its thickness vary from fifty to a hundred and fifty mono-atomic layers. Recently it was found (Long and Meyer²²) that also in the comparatively thin film, which is adsorbed at pressures well below the saturated vapour pressure, superfluidity sets in below the λ -temperature. The superflow remains, however, very small even at relative pressures of 0.95, where it is still less than 10 per cent of the flow of the saturated film (Mendelssohn). In order to decide whether this large variation of the superflow with the relative pressure is caused simply by a variation of the film thickness or by other factors, such as for instance the creep velocity of the film, the adsorption isotherm must be known with some accuracy, particularly in the region of high relative pressures. The latter pressure region is of interest for still another reason: it may yield information with respect to the question whether quantum effects are, or are not, of primary importance as regards the origin of the helium film. Unfortunately there is some disagreement between the results of different workers. Kistemaker²³ estimates from his experiments a thickness of thirty layers but a re-evaluation of his data indicates a multiple of this number at a relative pressure of 0.99. Long and Meyer find that the film is about eight layers thick, when the temperature is above 2.19 degrees: at lower temperatures, however, the adsorption was found to be anomalously high when the relative pressure rose above 0.90. Close to the saturation pressure, but still definitely below it, an adsorption corresponding with a hundred and sixty layers was claimed. Optical determinations, by Jackson and co-workers, of the thickness of the saturated film indicate, on the other hand, thicknesses which are only a third of those found by Long and Meyer and these results are in reasonable agreement with the very recent determinations of Bowers²⁴ and of Brewer and Mendelssohn²⁵).

In this chapter we shall describe an experimental determination of the adsorption isotherm on a glass surface according to a method which is in principle the same as that employed by Kistemaker. Because of the nature and the shape of the adsorbing surface, the influence of capillary condensation is reduced to a minimum. A number of modifications in the method were introduced in order to improve the accuracy. A description has also been given of a new differential gauge which has a sensitivity of about 0.1 microns Hg differential pressure at a mean pressure of a few mm. Hg. ²⁶⁾

As a result of our measurements and those of other workers we conclude that quantum effects are probably of secondary importance with respect to the origin of the helium film.

A brief survey of some theories of adsorption will now be given.

The theory of multilayer adsorption developed by Brunauer, Emmett and Teller ²⁷⁾, has met with considerable success in dealing with the characteristics of many adsorption isotherms. Moreover, the surface areas that can be obtained by applying the B.E.T. theory to adsorption measurements in the region of one monolayer are consistent with those found by means of quite different methods. It has been recognized nevertheless, that the B.E.T. isotherm, when it is fitted to the experimental data in the region of one monolayer deviates appreciably both above and below that region. In figure 11 we have represented the experimental isotherm in a typical case along with the theoretical one. The discrepancy at low relative pressures is usually ascribed to surface inhomogeneity of the adsorbent, an effect that is not taken into account by the original B.E.T.-theory. The disagreement at high relative pressures is of a more fundamental nature and is due to oversimplification in the assumptions of the B.E.T. theory. These assumptions are:

1. The number of molecules adsorbed on a given site is independent of the number adsorbed on adjacent sites.
2. The adsorption energy in all layers except the first is equal to the energy of liquefaction E_{liq} .

According to the first assumption the thickness of the adsorbed phase may show large fluctuations from site to site; this cannot correspond to reality, for in the actual case this would be opposed by the surface tension. Mc Millan and Teller ²⁸⁾ have shown that when the surface tension is taken into account without altering the second assumption the predicted adsorption becomes less than that found experimentally. This is a consequence of the insufficiency of assumption 2 which in itself gives too low an adsorption.

Halsey²⁹⁾ pointed out that in the absence of cooperative effects no new layer is likely to be formed before the underlying layer is complete: according to this view, then, multilayer gas adsorption is due to the fact that long range forces emanating from the adsorbent influence the energy of adsorption also in layers higher than the first, so in most cases the energy of adsorption in these layers will be larger than E_{liq} . This circumstance favours a larger adsorption and so the decrease in adsorption which is due to the surface tension is partly compensated.

Hill³⁰⁾ has considered the action of the van der Waals forces between the adsorbent and the adsorbed phase. In order to show clearly the assumptions involved, we shall briefly indicate his calculation of the isotherm.

Let the adsorbed film be considered as a plane slab of liquid with surface area S , uniform thickness h , and uniform number density ρ_1 of the molecules; the number density of the molecules in the adsorbent will be denoted by ρ_2 . It will be assumed that ρ_1 and the usual molecular distribution function $g(r)$ are the same in the slab as in the bulk liquid. Let F be the Helmholtz free energy of the slab in its equilibrium position in the presence of the adsorbent and let F_0 refer to the slab imbedded in the bulk liquid. $F - F_0$ is then the reversible isothermal work done on the system in

- 1) breaking a column of liquid of area S at $z = 0$ and removing the $z < h$ (W_1);
- 2) breaking the remaining liquid at $z = h$ and removing the part $z > h$ (W_2);
- 3) bringing the slab $0 < z < h$ up to its equilibrium position next to the adsorbent (W_3);
- 4) rejoining the parts $z < 0$ and $z > h$ of the bulk liquid (W_4).

By equating the molecular free energies of the vapour and the adsorbate we find:

$$kT \ln p/p_0 = \partial(W_1 + W_2)/\partial N$$

While the calculation of W_2 is straightforward, that of W_3 will depend on the suppositions made with respect to the nature of the adsorbent. A very simple assumption is that the adsorbent is structureless and that it does not perturb $g(r)$.

As regards the first layers, the latter assumption is certainly very crude but owing to the long range of the forces the influence of the higher layers, for which the assumption may be justified, will be quite comparable with that of the first.

When we write for the interaction energy between two molecules of the liquid:

$$u_{11}(r) = \epsilon_{11}(d_{11}/r)^{12} - 2 \epsilon_{11}(d_{11}/r)^6$$

and for that between a molecule of the liquid and a molecule of the adsorbent,

$$u_{12}(r) = \epsilon_{12}(d_{12}/r)^{12} - 2 \epsilon_{12}(d_{12}/r)^6$$

the following expression is found for the adsorption isotherm in the case that the thickness of the adsorbed layer is at least several molecules,

$$- \ln p/p_0 = \pi/3kT [\rho_1^4 d_{11}^6 \epsilon_{11} - \rho_1^3 \rho_2 d_{12}^6 \epsilon_{12}]$$

Introducing the molecular cross section σ , the number of adsorbed layers n and taking into account that approximatively $\rho_1 = \rho_2$ and $d_{11} = d_{12}$ we obtain the relation,

$$- \ln p/p_0 = \pi/3 \rho_1^4 d_{11}^6 \sigma_1^3 \frac{\epsilon_{11} - \epsilon_{12}}{kT} \frac{1}{n^3}$$

which is of the form,

$$- \ln p/p_0 = K/n^p$$

$$\text{where } K = \pi/3 \rho_1^4 d_{11}^6 \sigma_1^3 \frac{\epsilon_{11} - \epsilon_{12}}{kT} \quad \text{and} \quad p = 3$$

The power of n , n^p , which appears in the formula, is a direct consequence of the dependence on the distance of the attractive forces between the adsorbate and the adsorbent ($p = q - 3$, where $q = 6$ in the case of van der Waals forces). A similar power with law, $p = 2.6$, had previously been found empirically, by Halsey.

McMillan and Teller have shown that K is of the order of $(E_1 - E_{liq.})/RT$ where E_1 is the energy of adsorption of the first layer, $E_{liq.}$ is the energy of liquefaction and R the gas constant. The quantity $(E - E_{liq.})/RT$ appears also in the B.E.T. equation, which reads

$$\frac{m}{m_1} = \frac{Cp}{(p_0 - p)[1 + (C - 1)p/p_0]}$$

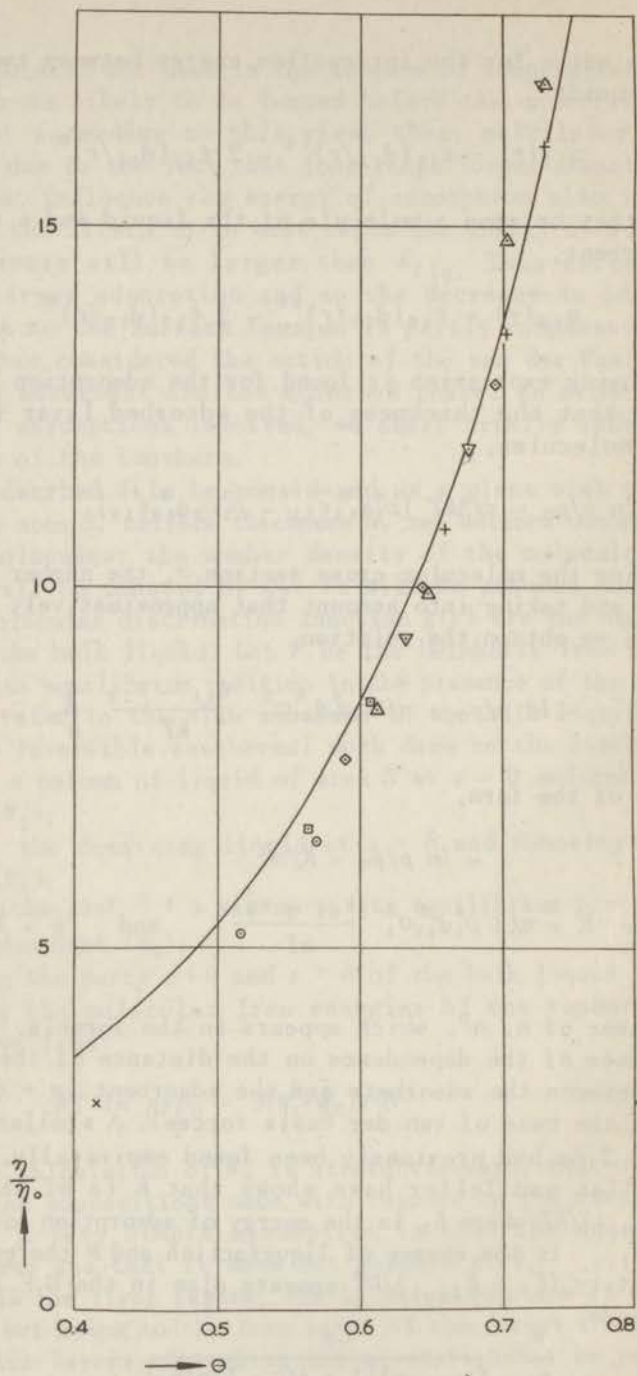


Fig. 10 Adsorption isotherm in a typical case

where m is the adsorbed mass at the given pressure p , and temperature, p_0 the pressure of the saturated vapour m_1 the mass of the first adsorbed layer and C an energy constant which is approximately equal to $C = \exp.(E_1 - E_{liq.})/RT$.

The film thickness at relative pressures close to saturation is according to the B.E.T. formula,

$$n_{B.E.T.} = \frac{A}{- \ln p/p_0}$$

where A is the ratio between the density of the first adsorbed layer and that of the higher layers, so $A = 1$. The Hill formula, on the other hand, yields,

$$n_{Hill} = \left(\frac{K}{- \ln p/p_0} \right)^{1/3}$$

where $K^{1/3} = 1$. It is seen that $n_{B.E.T.}$ is considerably larger than n_{Hill} which is due to the neglect of the surface tension by the B.E.T. theory. When the surface tension is allowed for in the latter theory, the number of adsorbed layers becomes according to McMillan and Teller

$$n_{M.T.} = \left(\frac{B}{- \ln p/p_0} \right)^{1/3}$$

where $B = kT/18\pi\epsilon d^2$, ϵ being the surface energy per unit surface of the semi-infinite liquid and d being the intermolecular distance. Because approximately $B^{1/3} = 0.1$ the number of adsorbed layers according to the above equation is much less than that predicted by the Hill formula which latter has been well confirmed by experiment (Dowers). In the case that the gas is adsorbed on a vertical surface, we may account for the influence of gravity by putting,

$$p = p_0 \exp.(-Mgz/RT)$$

where M is the molecular weight, R the gas constant and z the height of an element of the adsorbing surface above the surface of the liquid. Thus the following expression is obtained,

$$n = \frac{K^*}{z^{1/3}}, \text{ the value of the constant being, } K^* = \left(\frac{KRT}{Mg}\right)^{1/3}$$

We see therefore that in the case of adsorption by London-van der Waals forces, which is, for the rest, treated without specifically taking into account such effects as Bose-Einstein condensation or the zero-point energy, the thickness varies as the cubic root of the height above the level of the liquid (Schiff³¹).

Treatments which take explicit account of the influence of the statistics or the zero-point energy have been given by Bijl, de Boer and Michels, Band and Temperley³²). They generally obtain another dependence on the height z than that given above.

2. *Experimental arrangement.* As is well known there is some advantage in using a drawn glass surface; because of the absence of small cracks and fissures it is possible:

1. to identify the active surface area with the macroscopical one,
2. to avoid capillary effects, even at high percentages of the saturation.

Our apparatus comprised (see fig. 11):

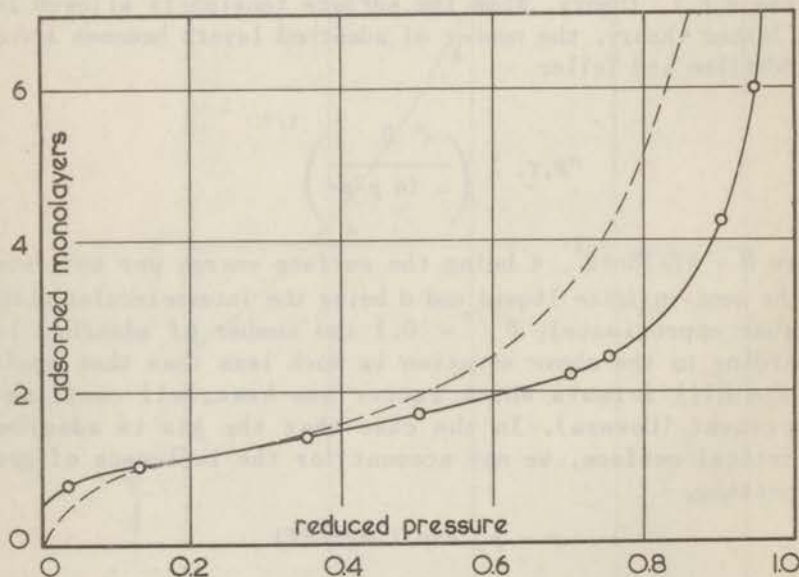


Fig. 11 Adsorption isotherm in a typical case.
 experimental curve
 B.E.T. curve

1. two vessels C which had approximately equal volumes but different internal surface areas. They were surrounded by a radiation shield R .
2. an oil differential gauge, G_1 , which served to measure the pressure inside the apparatus relative to the pressure of the bath,
3. a highly sensitive differential gauge, G_2 , which was connected with the adsorption cells C by means of glass tubes.

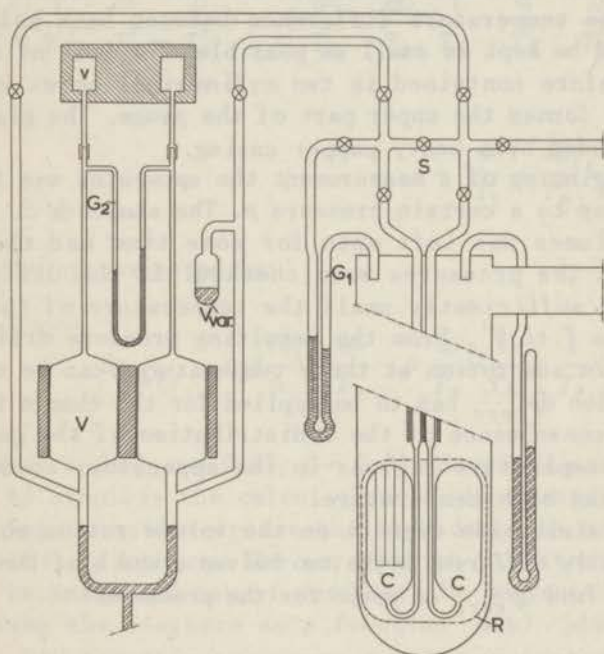


Fig. 12 Differential gauge and adsorption apparatus

As one will see from fig. 12, this device consisted essentially of two MacLeod gauges of identical construction, which we shall indicate by a and b . Each of the small volumes at the top was connected with either side of an oil differential gauge, G_2 . A small pressure difference could be amplified in this way. Differentiating the relation $p^* = p(1 + V/v)$ with respect to p , where p is the (mean) pressure, p^* is the amplified pressure and V and v are the large respectively the small volume of each MacLeod gauge, we find for the amplification factor:

$$f_d = f_m \left(1 - p \frac{V}{v} \frac{s_{\text{merc}}}{s_{\text{oil}}} \frac{dv}{dp} \right)$$

In this expression the factor $f_m = 1 + V/v$ gives the amplification of the mean pressure: s_{merc} and s_{oil} are the specific densities of mercury and oil and dv/dp is the volume increment as a consequence of a differential pressure. In order to ensure dependable readings the temperature difference between both halves of the gauge should be kept as small as possible. The bulk of the volumes v was therefore contained in two cylindrical bores in a copper block which formed the upper part of the gauge. The glass bulbs V were surrounded by a heavy copper casing.

At the beginning of a measurement the apparatus was filled with helium gas up to a certain pressure p . The stopcock S , connecting the two volumes was left open for some time and then closed, after which the pressures were checked. If the difference was found to be sufficiently small the temperature of the bath was changed from T to T' . From the resulting pressure difference the difference in adsorption at these temperatures can be calculated.

A correction dp_{corr} has to be applied for the change in pressure which is a consequence of the redistribution of the gas over the different temperature regions in the apparatus, accompanying a change in the bath temperature.

This redistribution depends on the volume ratios which are of course slightly different in the two halves a and b of the apparatus. In order to find dp_{corr} we write for the pressures:

$$p'_a = p \left(\frac{V_{a1}}{T_1} + \frac{V_{a2}}{T_2} + \frac{V_{a3}}{T_3} \right) \left(\frac{V_{a1}}{T_1} + \frac{V_{a2}}{T_2} + \frac{V_{a3}}{T_3} \right)^{-1},$$

V_{a1} is the geometrical volume at room temperature T_1 ,

V_{a2} is the volume of an adsorption cell at the temperature of the bath, T_2 respectively T'_2 ,

V_{a3} is the volume of the connecting tube at an 'effective' temperature T_3 , respectively T'_3 and

p_a and p'_a are the pressures corresponding with T_2 respectively T'_2 .

The analogous expression holds for p'_b . Assuming a constant temperature gradient along the connecting lines, we write:

$$T_3 = (T_1 - T_2)(\ln T_1 - \ln T_2)^{-1}$$

and introducing the volume ratios:

$$\alpha = \frac{V_{a2}}{V_{a1}}, \beta = \frac{V_{a3}}{V_{a1}}, \alpha + d\alpha = \frac{V_{b2}}{V_{b1}}, \beta + d\beta = \frac{V_{b3}}{V_{b1}}$$

we obtain

$$dp_{corr} = p_a \left(\frac{1}{T_1} + \frac{\alpha}{T_2} + \frac{\beta}{T_3} \right)^{-2} \left\{ \left(\frac{d\alpha}{T_2} + \frac{d\beta}{T_3} \right) \left(\frac{1}{T_1} + \frac{\alpha}{T_2} + \frac{\beta}{T_3} \right) - \right. \\ \left. - \left(\frac{d\alpha}{T_2} + \frac{d\beta}{T_3} \right) \left(\frac{1}{T_1} + \frac{\alpha}{T_2} + \frac{\beta}{T_3} \right) \right\}$$

which may be approximated by:

$$dp_{corr} = p_a \left(\frac{T_2'}{\alpha} \right)^2 \left(\frac{d\alpha}{T_1} - \alpha \frac{dT_2'}{T_3} \right) \left(\frac{1}{T_2} - \frac{1}{T_2'} \right) \quad 17$$

In our case we had: $\alpha = 0.97$, $\beta = 0.01$, $d\alpha = 0.01$ and $d\beta = -0.001$. In order to simplify the calculation of the adsorption we shall in first approximation ignore the dependence on temperature of the adsorption isotherm. The error which is introduced in this way will be small and may if necessary be corrected afterwards. Representing the isotherm as a function $\varphi(s)$ where $s = p/p_0$ is the reduced vapour pressure and taking into account that $s_a = s_b = s$ for the temperature $T(T_3)$, we obtain for the partial pressure difference due to the different adsorption at T and T' :

$$dp_{ads} = \{A_a \varphi(s'_a) - A_b \varphi(s'_b) - (A_a - A_b) \varphi(s)\} RT' / V$$

where φ is the mass of the adsorbed gas per unit surface, $V = V_a \approx V_b$, A_a and A_b are the adsorbing surface areas and R is the gas constant.

Introducing the differential surface area $A = A_a - A_b$ and considering that $p_b - p_a = dp_{ads} + dp_{corr}$ we find:

$$dp_{ads} = \left\{ -A_a \frac{\partial \varphi}{\partial s} \frac{dp_{ads} + dp_{corr}}{p_0} + A(\varphi(s'_b) - \varphi(s')) \right\} \frac{RT'}{V}$$

$$= (1 + A_a \frac{\partial \varphi RT'}{\partial s p_0 v})^{-1} \left\{ -A_a \frac{\partial \varphi}{\partial s} \frac{dp_{corr}}{lp_0} + A(s'_b - s_b) \right\} \frac{RT'}{V} \quad 18$$

When the slope of the isotherm is comparatively small we may omit the terms containing $\partial \varphi / \partial s$ in the expression for dp_{ads} .

3. *Results.* The calibration of the differential gauge yielded the following data:

$f_m = 15.0$ (approximately $V \approx 100 \text{ cm}^3$ and $v \approx 7 \text{ cm}^3$)

$f_d = 14.2$ for $p=0.13 \text{ cm Hg}$,

11.1 for $p=0.90 \text{ cm Hg}$.

For any other pressure f_d may then be found from formula (16). Readings scattered about $0.1 \mu \text{ Hg}$ at a mean pressure of 0.1 cm Hg and about $0.3 \mu \text{ Hg}$ at 1 cm Hg .

The large volume was approximately 100 cm^3 , while the small volume was 7 cm^3 . The diameter of the *K*-gauge G_2 was 0.1 cm ; it was filled with butylphthalate.

In order to adjust the dead space in the differential gauge to that of the adsorption cells the volume v_{var} was varied by means of filling part of it with mercury. The quantities α , β , $d\alpha$, $d\beta$ were then determined by means of separate runs at room temperature respectively at the boiling temperature of liquid hydrogen. The correction dp_{corr} calculated from formula (2) is of the order of a few microns Hg . In order to avoid the possibly large uncertainties in the calculation of dp_{ads} as indicated by (3), the determinations at high saturation percentages were carried out by means of desorption measurements: s' was then always situated in the saturation range where corrections for the slope of the isotherm may be neglected. In plotting the isotherm it was assumed that the adsorption at the lowest saturation, $s = 0.03$, was $0.07 \text{ cm}^3 \text{ S.T.P./m}^2$, which value was obtained by averaging the results of various investigators³³). No appreciable error will be involved, because

- a) the adsorption at such a low relative pressure is very small,
- b) capillary effects will not have much influence, even in the case of porous adsorbents.

As in the earlier measurements the differential surface area was 300 cm^2 . The results have been plotted in fig. 12. The cor-

responding temperatures, saturations and differential pressures (dp_{ads}) have been assembled in table IV. The curve represents all adsorption isotherms in the temperature range from 2.19 °K to 1.54 °K, because no temperature dependence could be detected within the limits of accuracy.

TABLE IV

The differential pressure, dp_{ads} , as a function of T , T' , s and s'				
T °K	T' °K	s	s'	dp_{ads} μ Hg
1.69	1.77	0.99	0.72	4.4
1.54	1.79	0.97	0.42	4.3
1.54	1.78	0.97	0.43	3.8
1.77	2.11	0.98	0.42	6.3
3.98	2.11	0.03	0.30	-6.6
3.98	1.78	0.03	0.68	-6.0
1.54	2.17	0.99	0.15	7.6
3.73	1.54	0.03	0.16	-0.7
3.73	1.33	0.03	0.43	-2.0

4. *Discussion.* We have indicated the number n of adsorbed statistical layers on the axis at right in fig. 12. With respect to the density of adsorbed helium we assumed that:

1. its value is in the first layer about four times the value of the bulk liquid,
2. its value is equal to that of the bulk liquid in the other layers; the latter assumption has a somewhat arbitrary character but has the advantage of being simple.

As will be seen, the number of adsorbed layers remains comparatively small even at a saturation of 0.99. This is in general agreement with the recent results of Brewer and Mendelssohn and of Bowers and in disagreement with those of Long and Meyer. We may also compare our results with those of Burge and Jackson³³⁾ who used an optical method. They found that the thickness d of the Rollin film at a height z above the liquid level could be represented by:

$$z = \text{Const.}/d^j$$

in which expression j varied from 2.5 to 3.5 as a function of temperature. This value suggests that the thickness of the film varied roughly as the cubic root of the height, according to the eq. given by Hill. The corresponding constant K has then approximately the value $K \approx 2$. Assuming the Hill relation to be valid in our case, we find approximately $K \approx 5$, which is less than the value given by Bowers, according to whom $K \approx 10$; he uses, however, aluminium as an adsorbent. When the results of gas adsorption measurements are compared with those obtained with the optical method for temperatures above the λ -temperature an appreciable discrepancy is found. One would sooner have expected the classical relation 2 to fit the experiments in this region better than below 2.186 °K. A plausible explanation seems to be that in those optical determinations where no mobile film was present a small temperature difference existed between the mirror and the liquid. A few thousandths of a degree K would be sufficient to reduce the relative pressure at the surface of the mirror to a value consistent with 2. An analogous argument might apply to the measurements of Long and Meyer in which they observed a very thick adsorbed film even at relative pressures $p/p_0 < 1$, when the temperature was below the λ -point. This large adsorption might be explained by the occurrence of capillary condensation, a possibility, which taking into consideration their experimental arrangement cannot be ruled out.

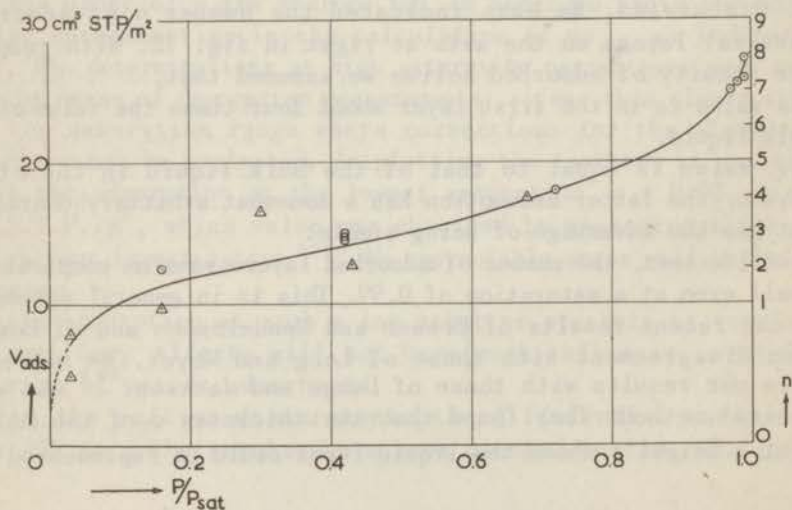


Fig. 13 Δ and \odot have been used to indicate points obtained by adsorption, respectively desorption measurements.

SAMENVATTING

In dit proefschrift worden de resultaten beschreven van:

- 1e. Een onderzoek naar de invloed van dichtheid en temperatuur op het impulstransport in He I.
- 2e. Een onderzoek naar de adsorptie van helium op glas bij temperaturen beneden het λ -punt.

Het doel van het eerste onderzoek was, gegevens te verkrijgen betreffende het impulstransport in vloeibaar helium bij temperaturen waar de invloed van quantumeffecten aanzienlijk is, maar niet zo overwegend dat een vergelijking met normale vloeistoffen zijn betekenis verliest. (Uit de merkwaardige verschijnselen, die in He II optreden, kan men de conclusie trekken, dat juist het impulstransport sterk beïnvloed wordt door de λ -transitie.)

In het eerste hoofdstuk wordt een kort overzicht gegeven van enige theorieën betreffende de viscositeit van dichte gassen en vloeistoffen.

In het tweede hoofdstuk wordt een methode³³⁾ beschreven volgens welke de viscositeit van He I werd gemeten bij drukken variërende van 10 tot 50 kg per cm². De gevonden waarden zijn geïnterpreteerd met behulp van een eenvoudig model, waarbij de moleculen worden beschouwd als harde bollen met een van de temperatuur afhankelijke straal. Op grond van dit model blijkt, dat He I wat zijn viscositeit betreft niet kan worden beschouwd als een verdund gas. Het is bij gevolg niet mogelijk de sterke daling van de viscositeit in de nabijheid van de θ -transitie op eenvoudige wijze te verklaren. Deze daling suggereert, dat de 'vrije weglengte' van de deeltjes (bij gelijkblijvende concentratie) toeneemt, naarmate hun thermische snelheid afneemt, (m.a.w. hun 'botsingsdoorsnede' wordt kleiner). Een soortgelijk verschijnsel schijnt op te treden in He II, zoals gesuggereerd wordt door de met dalende temperatuur toenemende viscositeit van het 'normale deel' bij temperaturen beneden 1.5 °K (zie fig. 4).

In het derde hoofdstuk wordt een manometrische methode beschreven²⁸⁾, waarmee de adsorptie van helium werd bepaald bij temperaturen beneden het λ -punt. Deze methode is in principe gelijk aan die welke gebruikt werd door Kistemaker bij zijn oriënterende metingen. Verschillende verfijningen stelden ons echter in staat

een grotere nauwkeurigheid te bereiken. Zo werd een differentiaal manometer ontwikkeld met een gevoeligheid van 0.01 micron Hg bij een totale druk in het adsorptie-toestel van de orde van 1 mm Hg.

Als resultaat van onze metingen vonden wij o.a., dat de geadsorbeerde laag een dikte had van 8 atoomdiameters bij een relatieve druk van 0.99, in redelijke overeenstemming met de uitkomsten van recente metingen, verricht door Brewer en Mendelsohn en door Bowers.

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Frederikse, H.P.R., Physica 15 (1949) 860; Thesis Leiden 1950; Strauss, A.J., Thesis Chicago 1952 (reviewed in Long and Meyer Advances in Physics 2 (1953) 1)

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CHAPTER I
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STELLINGEN

I

De opvatting dat He I wat zijn transporteigenschappen betreft met goede benadering als een verdund gas te beschouwen zou zijn, vindt geen steun in het experiment.

Tisza, L. C.R., Acad. Sci. Paris, **207** (1938) 1035, 1186
Phys. Rev. **72** (1947) 838

(Dit proefschrift p. 33)

II

Men mag aannemen, dat in de nabijheid van het λ -punt, de zelfdiffusie coëfficiënt van He I toeneemt bij dalende temperatuur.

(Dit proefschrift p. 33)

III

In de tot nog toe gegeven formuleringen van de theorie van Landau blijkt niet duidelijk waarom de impulsiedichtheid in een door He II lopende compressiegolf ongelijk nul is, in tegenstelling met wat in het algemeen het geval is.

Brillouin, L.M., Physica **5** (1925) 396

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Schoch, A., Z. Naturforschung **7a** (1952) 273

Kronig, R. and Thellung, A., Physica **18** (1952) 749

Borguis, F.E., Z. Physik **134** (1953) 273

Rev. Mod. Phys. **25** (1953) 653

IV

Het is niet waarschijnlijk, dat bij de adsorptie van helium beneden het λ -punt effecten een overwegende rol spelen, die door quantumstatistica moeten worden verklaard.

Brewer, D.F. en Mendelssohn, K. Phil. Mag. **44** (1953) 559

V

De wijze waarop Cox bij de microscopische beschrijving van revlisis-bele processen overgangswaarschijnlijkheden invoert, vereist nadere rechtvaardiging.

Cox, R.T., Rev. mod. Phys. **22** (1950) 238

VI

De wijze waarop in het leerboek van Goldstein de wetten van Newton worden ingeleid, is onbevredigend.

Goldstein, H., *Classical Mechanics* Cambridge 1950

VII

De resultaten van de susceptibiliteitsmetingen aan chroomkalium-aluin van Daniels en Kurti in de buurt van het Curiepunt zijn niet in overeenstemming met die van De Klerk, Steenland en Gorter. Volgens de verklaring, die Daniels en Kurti hiervan geven, zou de afwijking juist tegengesteld moeten zijn aan die in werkelijkheid optreedt.

Een verklaring is mogelijk, indien men rekening houdt met de wijze waarop de susceptibiliteit van het meetveld afhangt.

De Klerk, D., Steenland, M.J., Gorter, C.J., *Physica* 15 (1949) 649

Daniels, J.M., Kurti, N., *Proc. Roy. Soc. A* 221 (1954) 243

VIII

Het onderscheid dat Möller maakt tussen roosterwater en anion-water is overbodig.

Therald Möller, *Inorganic Chemistry* (New-York: John Wiley) p. 498

IX

Een gecoördineerd systematisch onderzoek zou aan te bevelen zijn in de Nederlandse en Buitenlandse archieven en bibliotheken, ten-einde een beter inzicht te krijgen in het Nederlandse muziekleven van vroeger.

X

Het is aan te bevelen bij de toelating van leerlingen tot de Middelbare Scholen in ruimere mate gebruik te maken van psycho-technisch onderzoek, dan thans het geval is.

