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Director of the Course

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Liquid Helium

1963

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XXI CORSO

a cura di G. CARERI
Direttore del Corso

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Foreword.

G. CARERI

Direttore del corso

Liquid Helium is a 53-year old subject. It started as the strangest liquid, now we realize it as the simplest liquid and a convenient system where new aspects of the many-body problem can be studied.

Therefore we felt that this school should be intended not as a repetition of the glorious past, but should provide the students with the background for the progress which is expected in the future.

The Varenna School is intended mainly for experimentalist research students, and in order to complement their preparation an emphasis has been given to theory at a level which can be familiar to them. Some seminars on contemporary aspects were also included to keep some unity between senior and junior investigators. Needless to say we did not expect to cover all the contemporary work in this field, but we tried to help the new generation to focus its attention on some open questions.

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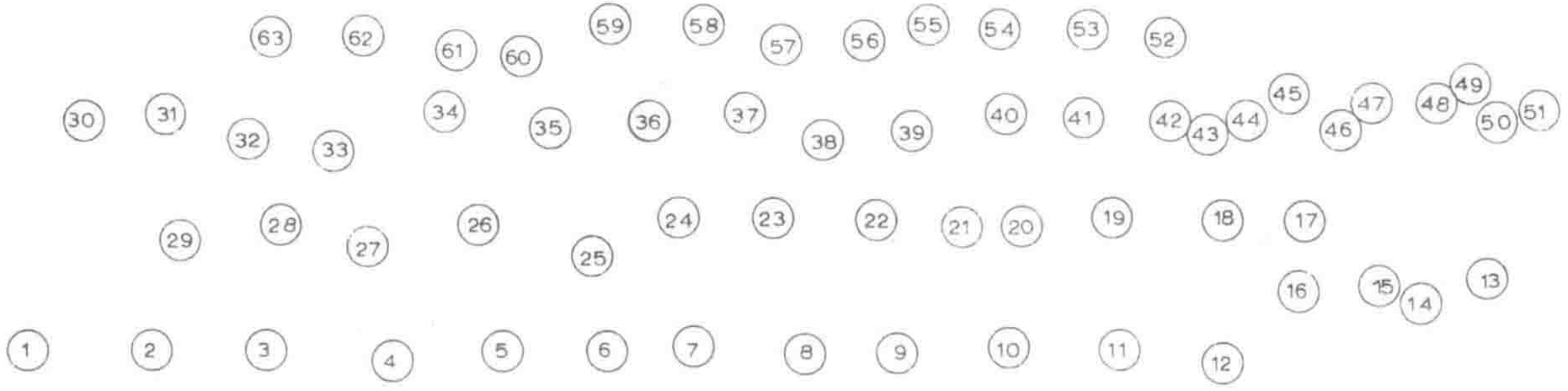

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LEZIONI

Excitation Model for Liquid Helium II.

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I. - Thermodynamic Properties of Liquid Helium.

1. – Discussion of diagram of states on the basis of the principle of corresponding states.

The exceptional position of the substance helium and in particular its condensed phase, can best be demonstrated by comparing its properties with those of the other noble gases and the hydrogen isotopes, which, in first approximation, can also be treated as a monoatomic substance. For such a comparison, in particular if quantum effects are under consideration, the appropriate method is a study on the basis of the principle of corresponding states using molecular units (1948) [1]. From the known values of the molecular parameters ε and σ characterizing the intermolecular potential field

$$\varphi(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^{6}]\,,$$

(r is the intermolecular distance, ε is the depth of the potential field at the minimum occurring at $r_{\text{min}} = 2^{\frac{1}{6}}\sigma$ and σ is the « diameter » for which $\varphi(\sigma) = 0$, *i.e.* the interaction energy changes sign), one derives « molecular units » for temperature ε/k, for molar volume $N_{\text{m}}\sigma^3$, for molar energy $N_{\text{m}}\varepsilon$ and for pressure ε/σ^3. For helium the values for these molecular units are:

TABLE I. – *Molecular units for* ^{4}He *and* ^{3}He.

$\varepsilon/k = 10.22\ {}^\circ\text{K}$ $\quad$ $N_{\text{m}}\sigma^3 = 10.06\ \text{cm}^3/\text{mol}$

$\varepsilon/\sigma^3 = 83.4\ \text{atm}$ $\quad$ $N_{\text{m}}\varepsilon = 84.9\ \text{J/mol}$

[$\varepsilon = 14.11 \cdot 10^{-16}$ erg $\quad$ $\sigma = 2.556$ Å]

The macroscopic properties for the various substances can now all be expressed in terms of these « molecular units », *e.g.* $T^* = kT/\varepsilon$, $V^*_{\mathrm{m}} = V_{\mathrm{m}}/N_{\mathrm{m}}\,\sigma^3$, $U^*_{\mathrm{m}} = U_{\mathrm{m}}/N_{\mathrm{m}}\,\varepsilon$, $P^* = P\sigma^3/\varepsilon$, etc.

In *classical theory* it can now easily be proved from dimensional considerations that, for instance, the reduced equation of state $P^*(V^*, T^*)$ should be the same for all monoatomic substances, provided they are properly described by the Lennard-Jones potential field $\varphi(r)$ and provided that the condition of additivity of intermolecular forces is satisfied. The consequence is that also characteristic quantities like *e.g.* the reduced critical temperatures T^*_{cr} and the reduced triple points temperature T^*_{tr}, the reduced critical molar volume $V^*_{\mathrm{m.cr}}$ and the reduced molar volume $V^*_{\mathrm{m.0}}$ and molar internal energy $U^*_{\mathrm{m.0}}$ at the absolute zero-point should be the same for the various substances.

In *quantum theory* this classical principle of corresponding states is no longer valid: again dimensional considerations show that as soon as Planck's constant h plays a role, the reduced equation of state takes the form $P^* = P^*(V^*, P^*, \Lambda^*)$, where $\Lambda^* = \Lambda/\sigma = h/(m\varepsilon)^{\frac{1}{2}}\sigma$ is a dimensionless quantity: the « quantum-mechanical parameter », which is essentially the ratio of a characteristic molecular de Broglie wave length $\Lambda = h/(m\varepsilon)^{\frac{1}{2}}$ to the diameter σ. When this quantum-mechanical parameter is small, quantum effects are negligible, but when Λ^* becomes larger quantum effects become more and more important.

For the heavy noble gases Λ^* is quite small: for Xe: $\Lambda^* = 0.064$, for Kr: $\Lambda^* = 0.102$ and for A: $\Lambda^* = 0.186$ showing that in these cases quantum effects are negligible. In fact these heavy substances satisfy very nicely the classical principle of corresponding states with $T^*_{\mathrm{cr}} = 1.26$, $T^*_{\mathrm{tr}} = 0.7$, $V^*_{\mathrm{m.cr}} = 3.25$, $V^*_{\mathrm{m.0}} \approx 0.9$, $U^*_{\mathrm{m.0}} \approx -8.6$.

For the lighter substances the quantum-mechanical parameter becomes larger and larger: $\Lambda^* = 1.22$ (resp. 1.73) for D_2 (resp. H_2) and reaches the extreme values $\Lambda^* = 2.67$ and 3.08 for ^{4}He, and ^{3}He, respectively.

These deviations from classical theory are illustrated in Fig. 1 by plotting the reduced critical temperature as function of the quantum-mechanical parameter Λ^*: one obtains thus a rather smooth curve and in fact this curve was used to predict in 1948 [2] the value of T_{cr} for ^{3}He before this substance was available for macroscopic measurements.

A similar plot of the reduced molar volume at absolute zero shows that the reduced molar volume increases from its classical value 0.95 to $(V^*_{\mathrm{m.0}})_{\mathrm{sol}} = 2.11$ and $(V^*_{\mathrm{m.0}})_{\mathrm{liq}} = 2.75$ for liquid ^{4}He and to the even higher value $(V^*_{\mathrm{m.0}})_{\mathrm{liq}} = 3.86$ for liquid ^{3}He: *as a result of quantum effects* the *light substances are thus « blown up » very much* to volumes 3 to 4 times of the corresponding classical value.

The quantum effect on the reduced internal energy is even more drastic. Here the reduced internal molar energy of the condensed phase, which is

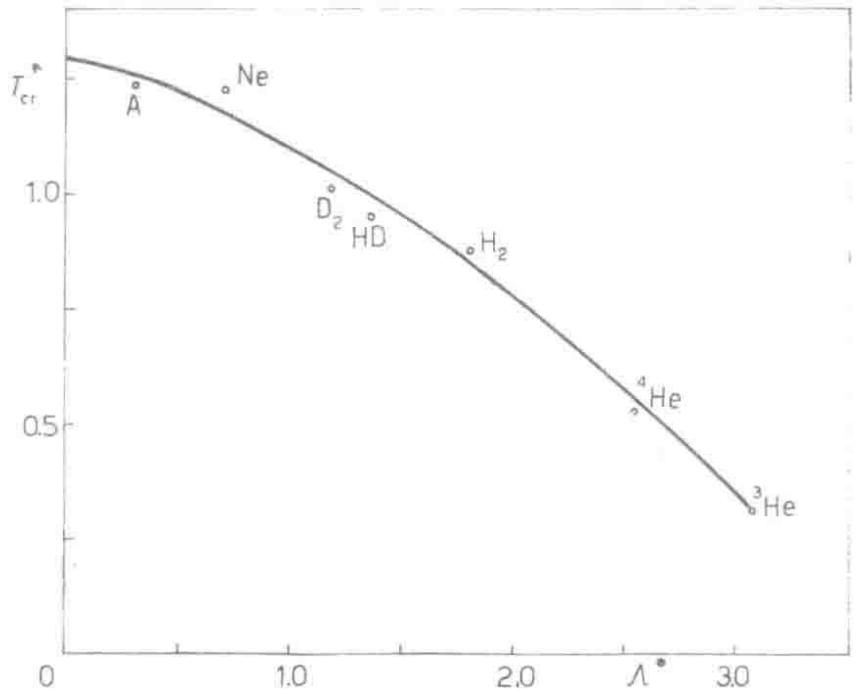

Fig. 1. – The reduced critical temperature plotted as function of the quantum-mechanical parameter Λ^* for various substances, showing the large influence of quantum effects in the case of ^{4}He and ^{3}He.

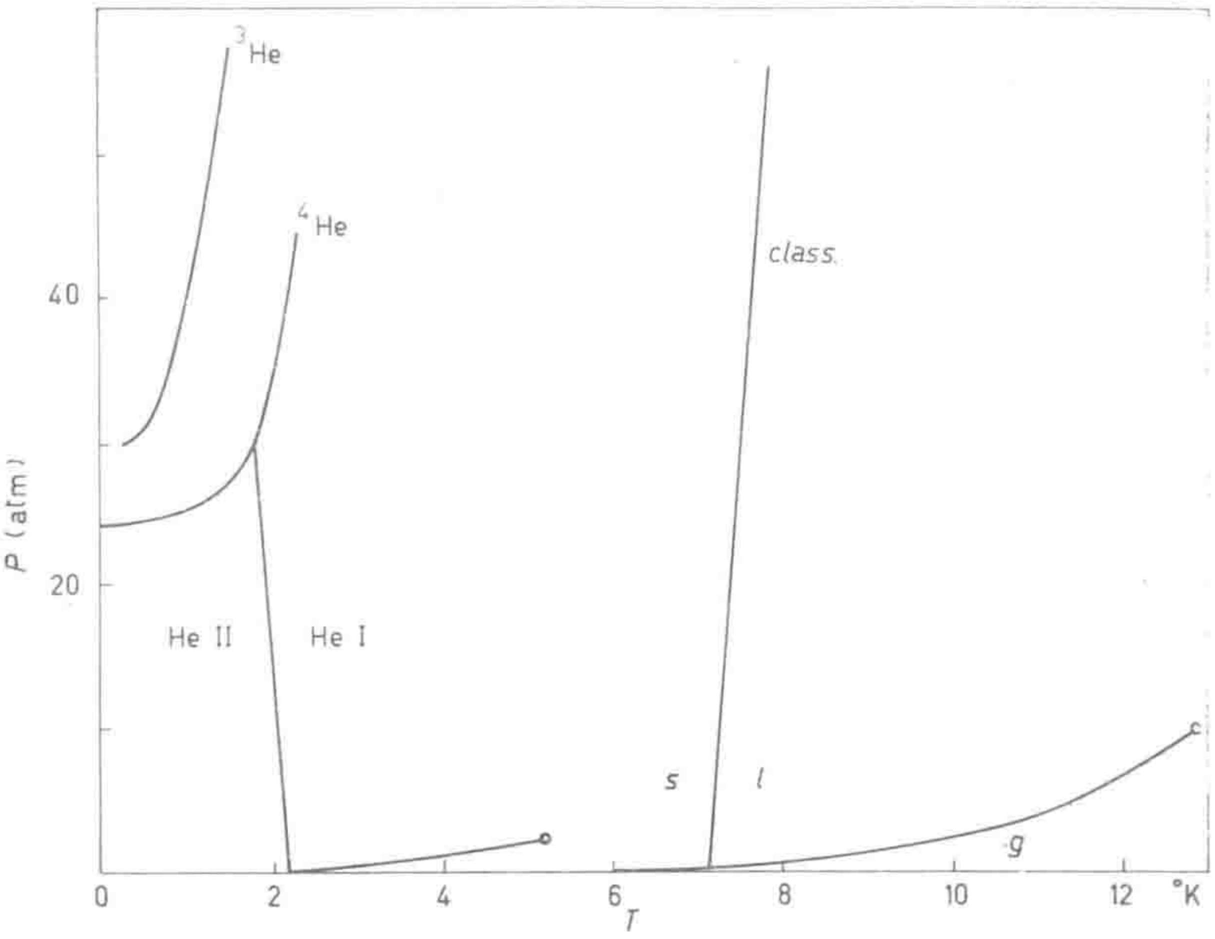

Fig. 2. – The diagram of states of ^{4}He and ^{3}He compared with the corresponding classical diagram of state.

$U^*_{m,0} = -8.6$ for classical substances changes gradually as Λ^* increases and reaches the value $(U^*_{m,0})_{liq} = -0.70$ for liquid ^{4}He and even $(U^*_{m,0})^*_{liq} = -0.25$ for liquid ^{3}He. The *reduced « binding energy » of the condensed phase is thus reduced by a factor larger than* 10 *as a result of the quantum effects.*

An overall picture of the large influence of quantum effects in the case of helium is obtained by considering the diagram of states for ^{4}He and ^{3}He in Fig. 2. In this diagram is also drawn the « classical » diagram of states which would have been the real one if quantum effects would have been absent. Besides a shift of the vapour pressure line describing the gas-liquid equilibrium and the critical point, the really drastic differences result from the big shift of the melting line to lower temperatures and higher pressure which leads to the disappearance of the overcrossing of melting line and vapour pressure line and thus also of the triple point, whith the consequence of the extension of the liquid phase down to the absolute zero. It is well known that in the case of ^{4}He there exists in the liquid phase a phase transition on the λ-line, which separates the two phases liquid He I and liquid He II.

2. – The zeropoint energy. Behaviour at $T = 0$.

A qualitative explanation of the exceptional position of liquid helium was given more than 30 years ago already by SIMON as being due to the zero-point energy. For a solid substance described by the Debye theory the total molar zeropoint energy connected with the zero-point oscillations of all the longitudinal and transversal elastic modes is given by

$$U_{m,z} = 3\int_0^{k_D} \frac{1}{2}\hbar ck\, d\boldsymbol{k}/8\pi^3 = \frac{9}{8}R\Theta_D\,, \tag{1.1}$$

where $\Theta_D = \hbar c k_D/k$ (c = velocity of sound). The « Debye circular wave number » $\boldsymbol{k}_D$ is defined as usual by

$$N_m = V_m\int_0^{k_D} d\boldsymbol{k}/8\pi^3 = V_m\cdot\frac{4}{3}\pi k_D^3/8\pi^3\,. \tag{1.2}$$

As the characteristic Debye temperature increases with decreasing volume, this zero-point energy increases also and consequently exerts an internal pressure which tends to blow up the substance. In classical theory the minimum energy occurs at the reduced volume: $V^*_{m,0} = 0.916$ at which the reduced potential energy of the close-packed structure (calculated with the Lennard-Jones interaction $\varphi(r)$) assumes the value $U^*_{m,0} = -8.610$. It si easy to verify [3] that the above mentioned zero-point pressure causes deviations from those values, which in first approximation are proportional to Λ^*. Also if one describes the solid phase and an Einstein solid, with all particles oscillating independently in the repulsive field of the surrounding particles, one obtains the same result: the zeropoint energy « blows up » the condensed phase and moves away the molecules from the lattice arrangement of minimum potential energy to regions of higher energy, thus causing the very large shift in the internal energy of ^{4}He and ^{3}He, found experimentally.

A very approximate picture for the co-existence of two phases, a solid and a liquid phase, at the absolute zero was given by LONDON (1936) [4]: Although at small molar volume (and higher pressures) the close-packed structure (with co-ordination number 12) has the lowest energy, the large zeropoint energy has the effect that at larger molar volumes and smaller pressure a « structure » with lower co-ordination number (about 6) has a lower energy and thus becomes stable. This then causes the phase transition from the high-pressure close-packed solid phase to the low-pressure liquid phase (at $P=25$ atm for ^{4}He and about 30 atm for ^{3}He) which certainly has a much lower co-ordination number (although this is a somewhat vague concept for quantum liquids like ^{4}He and ^{3}He!).

3. – Caloric properties.

After this rather qualitative description of the situation at the absolute zero of temperature, we now turn to a brief survey of the caloric properties at nonzero temperatures. In Fig. 3 the molar heat capacity for ^{4}He and ^{3}He is drawn as function of temperature. For ^{4}He at low temperatures ($T < 0.6$ °K) $c_v = aT^3$, with a value of $a = (16\pi^5 k^4/15h^3c^3)V$ corresponding to the low-temperature limit of a Debye solid with longitudinal waves only ($c = 238$ m/s). At temperature $T > 0.6$ °K the heat capacity rises exponentially and shows a phase transition at $T = 2.1$ °K. The exact behaviour of the heat-capacity curve in the vi-

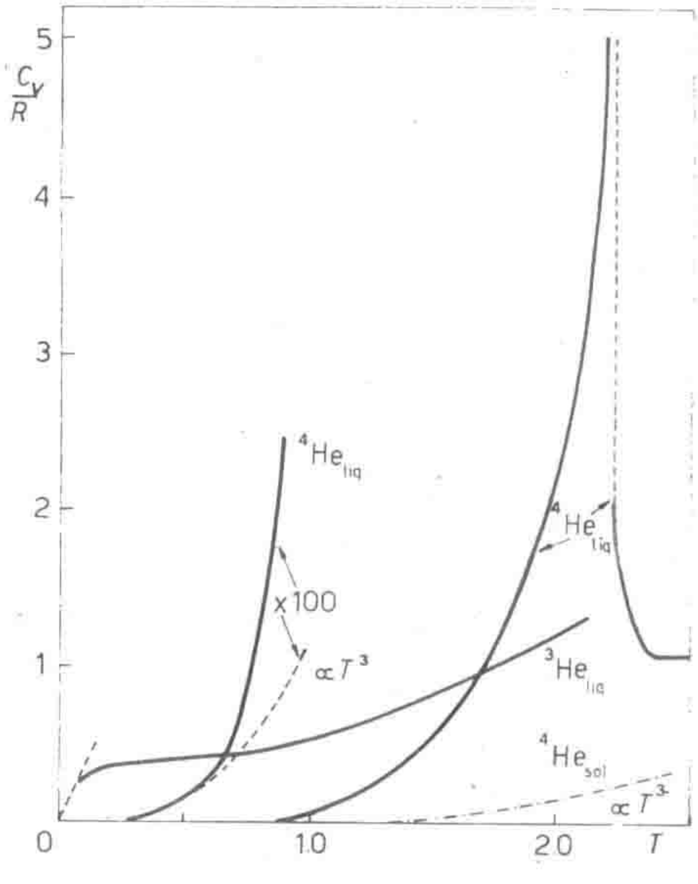

Fig. 3. – The molar heat capacity for liquid ^{4}He and ^{3}He.

cinity of the λ-point has been investigated in very much detail in particular by BUCKINGHAM and FAIRBANK (1957) [5]. There appears to exist a logarithmic infinity on both sides of the λ-point.

For ^{3}He the heat capacity appears to be linear $C_v = bT$ at very low temperatures ($T < 0.1$ °K) as it would be for an ideal gas of Fermi molecules. Using the value $b = (\pi^2 m^*_{\text{eff}} k^2/h^2) N (4\pi V/3N)^{\frac{2}{3}}$ for an ideal gas one finds an effective mass of about $2m_{\text{He}}$. For higher temperatures the curve deviates strongly from this linear curve. So far no singularity in the heat capacity has been found.

4. – Thermal expansion.

Both liquids ^{4}He and ^{3}He have a very remarkable behaviour of the thermal expansion coefficient as a function of temperature.

For ^{4}He the thermal expansion coefficient (see Fig. 4a) is proportional to T^3 and positive at low temperatures $T < 0.5$ °K, then the curve changes sign at 1.2 °K and between this temperature and the λ-point the thermal expansion is negative.

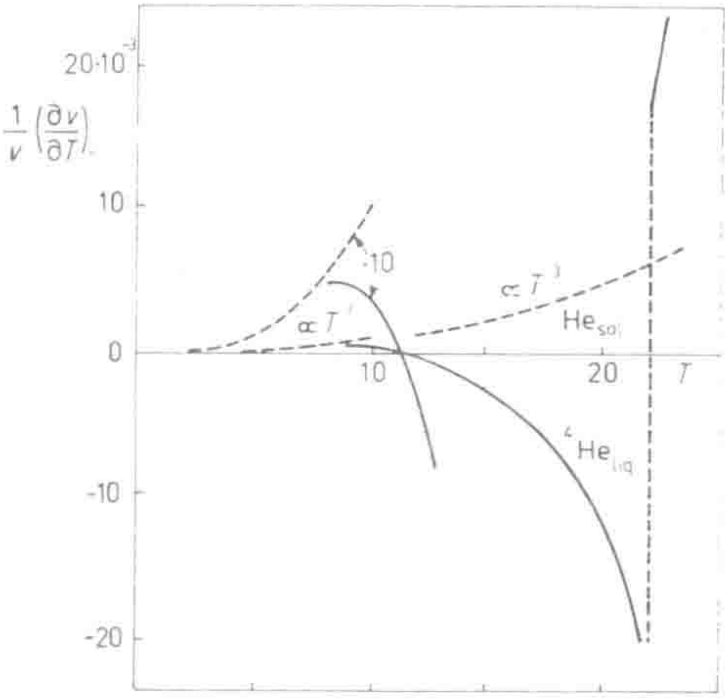

Fig. 4a. – The thermal expansion curve for liquid and solid ^{4}He. At temperatures below 1.3 °K the scale has been increased by a factor 10.

For ^{3}He the thermal expansion coefficient (Fig. 4b) becomes proportional to T and negative at very low temperatures $T < 0.1$ °K and then changes sign at 0.6 °K and remains positive for higher temperatures.

The behaviour can at least partly be understood using the thermodynamic relation:

$$(1.3)\quad \alpha = \\ = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \varkappa\left(\frac{\partial P}{\partial T}\right)_V = \varkappa\left(\frac{\partial S}{\partial V}\right)_T,$$

where $\varkappa = -(1/V)(\partial V/\partial P)_T$ is the compressibility.

This gives for ^{4}He at $T < 0.5$ °K:

$$(1.4)\qquad S = \frac{1}{3}\,aT^3\,, \qquad \alpha = \frac{1}{3}\,\varkappa a T^3\left|1 - 3\,\frac{\partial \ln c}{\partial \ln V}\right|,$$

and for ^{3}He at $T < 0.1$ °K:

$$S = bT\,, \qquad \alpha = \varkappa b T \left[\frac{2}{3} + \frac{\partial \ln m_{\text{eff}}}{\partial \ln V}\right]. \tag{1.5}$$

In agreement with the experimental facts for ^{4}He that $\partial c/\partial V < 0$, one finds a positive α, proportional to T^3 at low temperatures. At higher temperatures

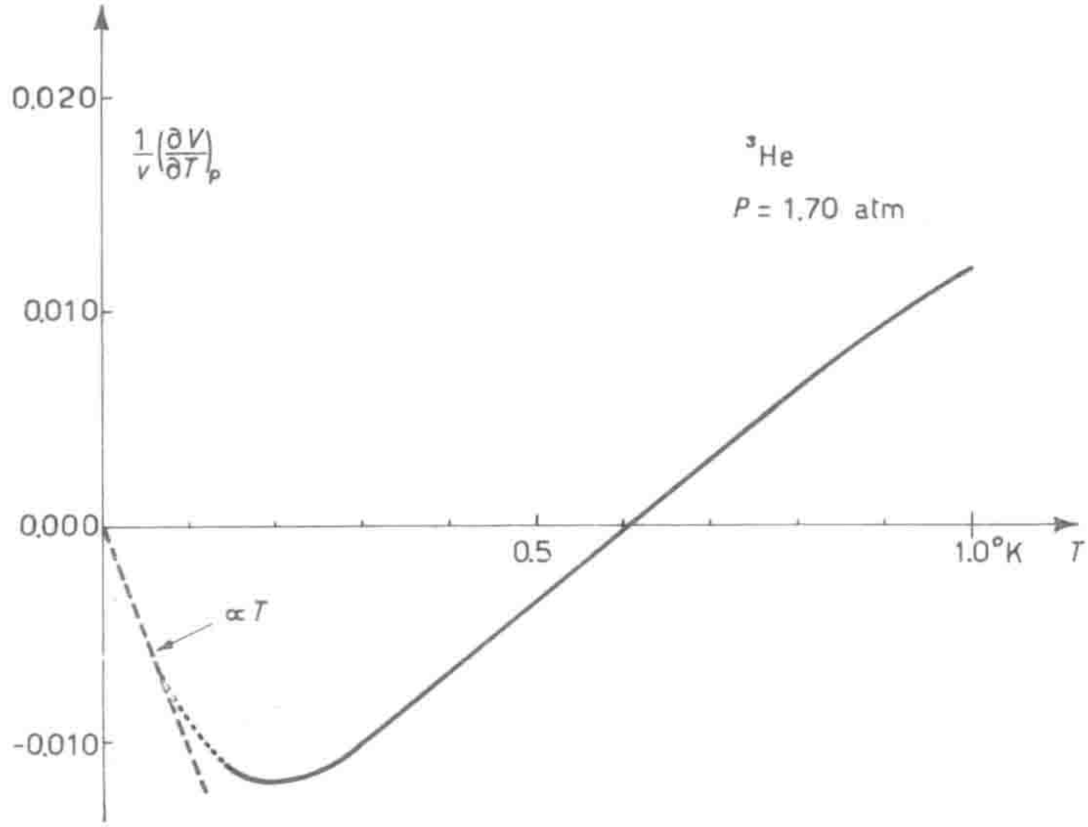

Fig. 4*b*. – The thermal expansion curve for liquid ^{3}He.

the abnormal thermal expansion coefficient shows that there $\partial S/\partial V$ must be negative. On the other hand the fact that experimentally for ^{3}He the thermal expansion coefficient is negative at very low T shows that $\partial \ln m_{\text{eff}}/\partial V < -\frac{2}{3}$, so that the effective mass should become larger on compression.

In the following lecture only the behaviour of ^{4}He will be considered more in detail from the theoretical point of view. The further theoretical discussion of the behaviour of liquid ^{3}He will be given by Prof. Sessler.

II. - Phenomenological Theory of Two-Fluid Model.

1. – The two-fluid model.

The origin of the two-fluid model for the description of the properties of liquid ^{4}He II came from two different directions. Tisza (1938) [6] starting from the analogy of the situation in liquid helium II with that existing in an ideal B. E. gas below its condensation temperature, suggested the two-fluid model and predicted the possibility of temperature (« second sound ») waves in liquid helium. LANDAU (1941) [7] developed a slightly different version of the two-fluid model, which on the end has proved to give a quite accurate description of the phenomena in liquid helium. We therefore now first present the basic assumptions on which LANDAU based the two-fluid model. For the purpose of describing the many reversible and irreversible transport phenomena occurring in liquid helium II, it is useful to introduce the concept of two interpenetrating fluids: the *superfluid* and the *normal fluid,* which can move with respect to each other practically without friction. The simplest properties to be attached to the two fluids were the following:

a) The *superfluid* moves *without friction* through capillaries and over surfaces as long as the velocity does not become larger than a so-called « critical velocity » the value of which is of the order of magnitude of $(1 \div 10)$ cm/s for flows through narrow tubes.

b) The *superfluid transports no entropy* as is shown by the well-known mechano-caloric effect: if liquid helium flows through narrow capillaries the heat $Q = TS$ is developed at the entry of the capillary and should be supplied at the exit again if we want to keep the flow isothermal. The same applies to the flow over surfaces.

c) The *normal-fluid density, i.e.* the mass density of the fluid which still behaves normal and which shows viscous friction has been determined by the famous experiment of ANDRONIKASHVILI (1946): a pile of discs, at a very small distance, hangs in the liquid attached to a torsion wire. During the oscillations around the axis which the pile of discs can carry out, the superfluid part remains at rest as this is not accelerated with the discs because of lack of friction (the velocities remain smaller than the critical velocities). From the determination of the oscillation period follows the moment of inertia of the whole system which oscillates, and from that one can obtain the normal fluid density as a function of temperature. Later more experiments of this character have been carried out, which confirm the early experiments of Andronikashvili. A direct confirmation of these data came from the superfluid wind tunnel experiments of PELLAM and collaborators which gave directly the superfluid density as a function of temperature. The most accurate data have been obtained, however, in an indirect way from the experiments on second sound (see Section **3** of this chapter). The ratio of the normal fluid density ϱ_n to the total mass density ϱ, plotted as a function of temperature, is given in Fig. 5. At very low temperatures the curve goes to zero proportional to T^4 as is shown on an 10 000 × larger scale for $T < 0.6$ °K. At higher temperatures the curve rises exponentially up to $\varrho_n = \varrho$ at $T = T_\lambda$.

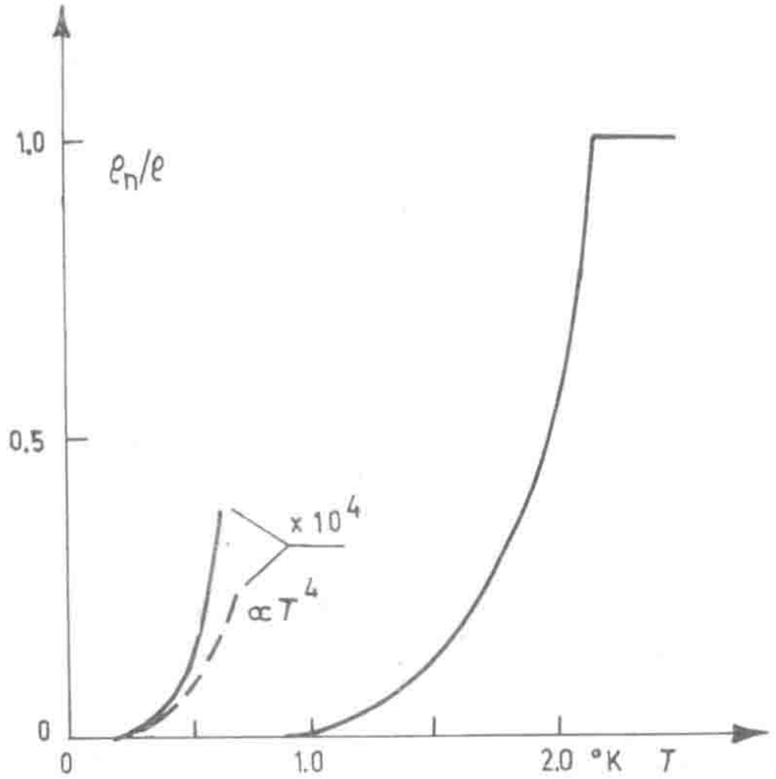

Fig. 5. – The ratio of normal density and total mass density as obtained from oscillating pile and from second sound experiments.

d) The *normal fluid part* shows ordinary liquid viscous behaviour. This follows from the damping of oscillating discs and oscillating cylinders in liquid helium: this damping can be interpreted in the usual way as the damping caused by a fluid of *viscosity* η and of density ϱ_n. The viscosity coefficient appears to show no singular behaviour at the λ-temperature: when the temperature decreases the viscosity decreases also, goes through a minimum of about 12 μP at 1.5 °K and then increases again, the value at 0.8 °K being already about 70 μP.

The heat conduction through liquid helium is a much more complicated phenomenon as this is the result of a flow of superfluid from the low- to the high-temperature region combined with a viscous streaming of normal fluid from the high- to the low-temperature side. This is quite contrary to the usual heat conduction in a liquid where no macroscopic flow occurs. In narrow channel this heat current becomes proportional to the temperature gradient but the size is not determined by the heat-conductivity coefficient but by the inverse of the viscosity.