Superfluidity and Superconductivity

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VAN NOSTRAND REINHOLD COMPANY
New York - Cincinnati - Toronto - London - Melbourne

VAN NOSTRAND REINHOLD COMPANY LTD
25–28 Buckingham Gate, London S.W.1

INTERNATIONAL OFFICES
New York Cincinnati Toronto Melbourne

ISBN 0 442 30015 8 cloth
ISBN 0 442 30016 6 paper

Library of Congress Catalog Card No. 73–11584

Printed in Great Britain by
Butler & Tanner Ltd, Frome and London

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Chapter 1

Superfluids and Macroscopic Quantization

1.1 Basic properties of liquid He^4

The two isotopes of helium have the lowest normal boiling points of all known substances, 4·21 K for He^4 and 3·19 K for He^3. When the temperature is reduced further, both He^3 and He^4 remain liquid under the saturated vapour pressure, and would apparently do so right down to absolute zero. To produce the solid phases requires application of a rather high pressure, 25 atmospheres or more (Figs. 1.1 and 1.2).

This reluctance of helium to condense arises from a combination of two factors, the low mass of the atoms and the extremely weak forces between them. The forces are weak because of the simplicity and symmetry of the helium atom with its closed shell of two electrons and the absence of dipole moments except for the small magnetic moment of the He^3 nucleus. The effect of low atomic mass is to ensure a high value of zero-point energy, as may be seen from the following argument.

At a given instant of time, one particular atom in liquid He^4 occupies a certain volume bounded by the atoms immediately surrounding it. Owing to the motion of the atoms, this volume varies, but we can say that, on average, the atom is contained within a sphere of volume equal to the atomic volume V_a, and that the sphere has radius $R \sim V_a^{1/3}$. From the quantum-mechanical uncertainty relation, it can be inferred that a particle inside such a cavity has an uncertainty in its

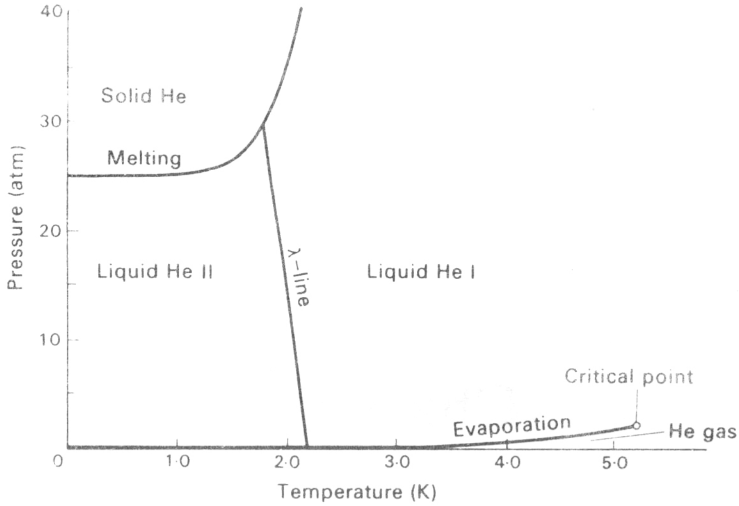

FIG. 1.1 Phase diagram of He^4 (after London 1954).

momentum $\Delta p \sim h/R$, and, consequently, that it possesses kinetic energy of localization, or zero-point energy, $E_0 \sim (\Delta p)^2/2m_4 \sim h^2/2m_4 R^2$, where m_4 is the mass of a He^4 atom. In terms of the atomic volume $E_0 \sim h^2/2m_4 V_a^{2/3}$ and this dependence of E_0 upon V_a is shown schematically in Fig. 1.3. Calculation of the potential energy of the liquid is not easy, and depends upon the choice of model interaction

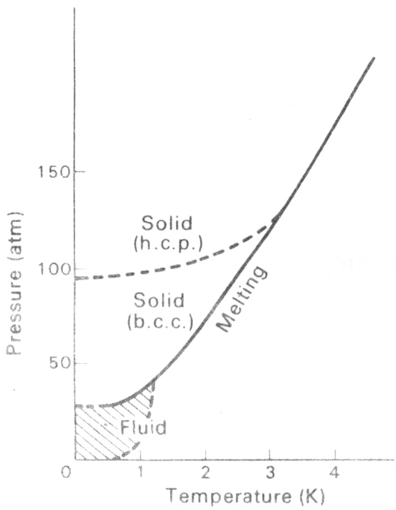

FIG. 1.2 Phase diagram of He^3 (after Grilly and Mills 1959). Hatched area shows region of negative expansion coefficient.

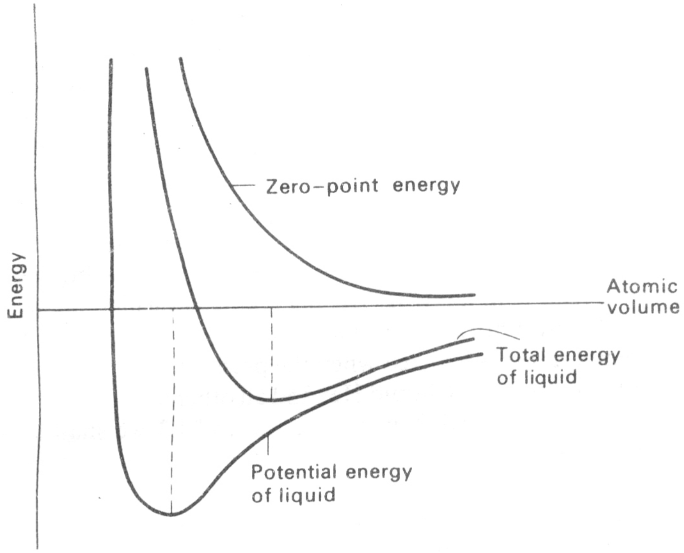

FIG. 1.3 Energy of liquid helium. Total energy is sum of potential energy and zero-point energy.

between two atoms, but it will have the general form of the lowest curve in Fig. 1.3. Because m_4 is small, the zero-point energy is comparable in magnitude to the minimum in the potential-energy curve. The result is that the total energy of the liquid reaches a minimum at a considerably greater atomic volume than the potential-energy minimum. Thus the interatomic forces are strong enough to produce the liquid phase at a low enough temperature, but the high zero-point energy keeps the density of the liquid rather small.

This qualitative argument may be extended to the formation of solid helium. The potential minimum for a lattice will occur at smaller atomic volume than for the liquid (Fig. 1.3), but here the zero-point energy is so large that the lattice is unstable unless a large external pressure is applied. The arguments we have used apply equally to liquid He^3, which has a lower atomic mass and in which the effects of zero-point energy are consequently even greater. Hydrogen is not comparable because the H_2 molecule is much more easily polarized than the single He atom, with the result that the van der Waals force between two H_2 molecules is twelve times stronger than that between two He atoms. In hydrogen, therefore, the binding forces far outweigh the zero-point energy and the solid phase is the stable one at absolute zero. Since all other substances are heavier than hydrogen and have stronger van der Waals interactions, it follows that helium is unique in remaining liquid at indefinitely low temperatures.

Immediately below their respective boiling points, both He^3 and He^4 behave as ordinary liquids with small viscosity. However, at 2·17 K liquid He^4 undergoes a change which is not shared by He^3. This transition is signalled by a specific heat anomaly, whose characteristic shape (Fig. 1.4) has led to the name λ-point being given to the temperature (T_λ) at which it occurs. Furthermore, observation of the liquid at the instant that its temperature is reduced below T_λ reveals a remarkable alteration in its appearance. Liquid helium is maintained at temperatures below 4·2 K by lowering the vapour pressure above the helium bath so that boiling occurs under reduced pressure. Above T_λ bubbles of vapour form within the bulk of the liquid in the customary way and the whole liquid is violently agitated as these rise to the free surface and escape. On the other hand, as soon as the transition point is reached, the liquid becomes quite still and no more bubbles are formed. We infer that T_λ marks the transition between two different forms of liquid He^4, known conventionally as Helium I above the λ-point and Helium II below it. On the phase diagram (Fig. 1.1) the regions in which the two forms are stable are separated by a broken line, which is not quite vertical, indicating that the transition temperature is lowered when the pressure is increased. The fact that He II is very different from He I, liquid He^3 and all other liquids, will become clear as we describe its thermal and flow properties. In § 1.3 we shall return to the λ-transition, which occupies a crucial place in the macroscopic theory of liquid He^4.

Experiments to determine the *viscosity* of He II can be divided into two classes: those designed to measure viscous resistance to flow, and those which detect the viscous drag on a body moving in the liquid. The results shown in Fig. 1.5 are typical of the former; the flow velocity through narrow channels of width varying between 0·1 μm and 4 μm is found to be almost independent of the pressure gradient along the channel. This suggests that the viscosity of He II is virtually zero, a conclusion that is supported by the persistent-current experiments of Reppy and Depatie (1964). In these a torus-shaped vessel was packed with porous material to provide very narrow channels for the liquid. The torus was rotated about its axis of symmetry and then brought to rest, after which the He II continued to flow, showing no reduction in angular velocity over a twelve-hour period, and indicating that He II can flow without dissipation.

On the other hand, experiments using oscillating disks (e.g. Keesom and MacWood, 1938), vibrating wires (Tough, McCormick and Dash, 1963), and rotation viscometers (e.g. Woods and Hollis Hallett, 1963; Fig. 1.6 in this book) demonstrate the existence of a viscous drag, consistent with a viscosity coefficient not much less than that of He^4 gas. It seems that He II is capable of being both viscous and non-viscous at the same time. This apparent contradiction is the essence of the *two-fluid model*, first suggested by Tisza (1938), in terms of which many of the properties of He II can be explained. According to this model, He II behaves as if it were a 'mixture' of two liquids, one, the normal fluid, possessing an ordinary viscosity, and the other, the superfluid, being capable of frictionless flow past obstacles and through narrow channels. To avoid any misunderstanding, it must be clearly stated at the outset that the two fluids cannot be physically separated; it is not permissible even to regard some atoms as belonging to the normal fluid and the remainder to the superfluid, since all He^4 atoms are identical. We therefore state the assumptions of the two-fluid model in the following way.

Below T_λ, liquid He^4 is capable of two different motions at the same instant. Each of these has its own local velocity, respectively $\mathbf{v}_n$ and $\mathbf{v}_s$ for the normal fluid

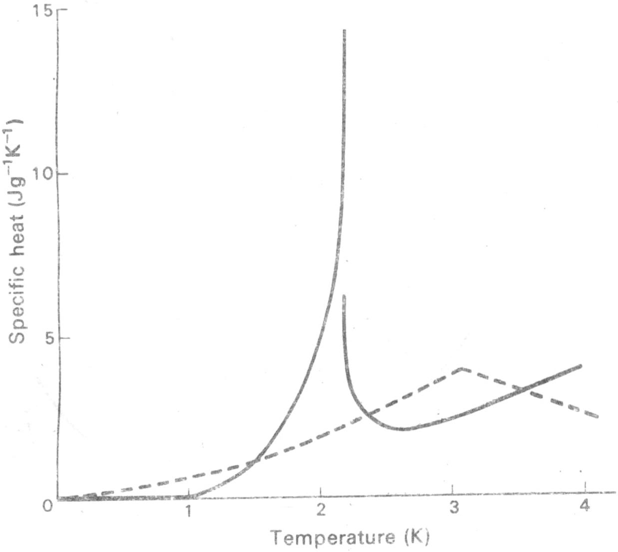

FIG. 1.4 Specific heat of liquid He^4 (after Atkins 1959). Broken line shows specific heat of ideal Bose–Einstein gas having same density as liquid He^4.

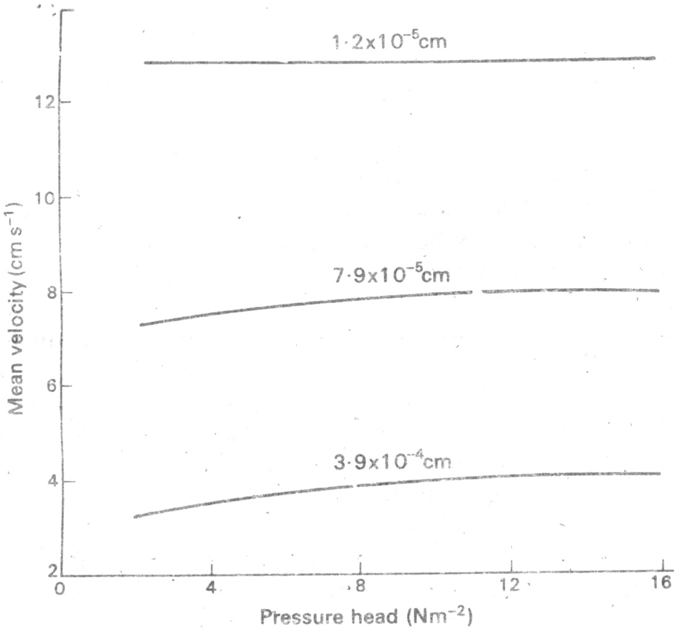

FIG. 1.5 Flow velocity of He II through narrow channels of various widths at 1·2 K. (After Allen and Misener 1939 and Atkins 1952.)

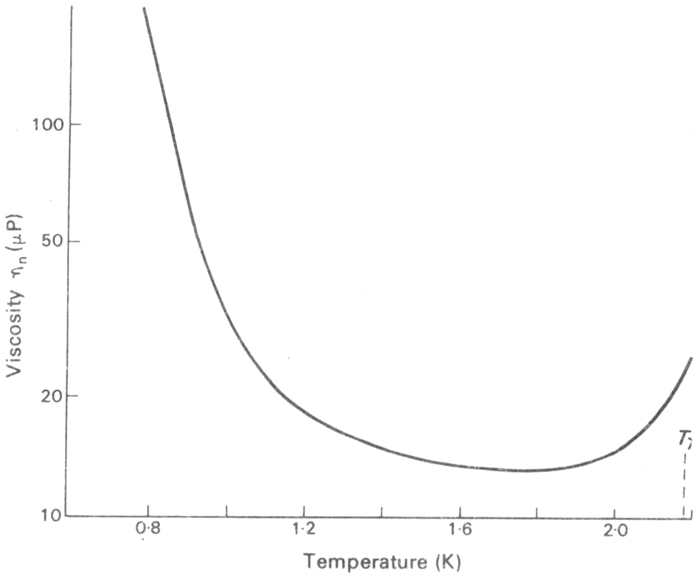

FIG. 1.6 Viscosity of He II measured in a rotation viscometer (Woods and Hollis Hallett 1963).

and the superfluid; likewise each has its own effective mass density, ρ_n and ρ_s. The total density ρ of the He II is therefore given by

$$\rho = \rho_n + \rho_s \tag{1.1}$$

and the total current density by

$$\mathbf{j} = \rho_n \mathbf{v}_n + \rho_s \mathbf{v}_s. \tag{1.2}$$

This approach in which the two fluids are treated independently is most useful when the velocities are small. At higher velocities, the superfluid flow becomes dissipative, the normal fluid exhibits turbulence, and there is the possibility of interaction between the two. When these factors are allowed for, the two-fluid equations become rather complicated.

The validity of the two-fluid model is most strikingly demonstrated in the experiment devised by Andronikashvili (1946). He used a pile of equally spaced thin metal disks (Fig. 1.7), suspended by a torsion fibre so that they were able to perform oscillations in liquid helium. The disk spacing was sufficiently small to ensure that above T_λ all the fluid between the disks was dragged with them. However, below T_λ the period of oscillation decreased sharply, indicating that not all the fluid in the spaces was being entrained by the disks. This result confirmed the prediction that the superfluid fraction would have no effect on the torsion pendulum. The experiment gave a direct method of measuring the variation of ρ_n/ρ with temperature (Fig. 1.7), and by inference ρ_s/ρ. We note that He II is almost entirely superfluid below 1 K.

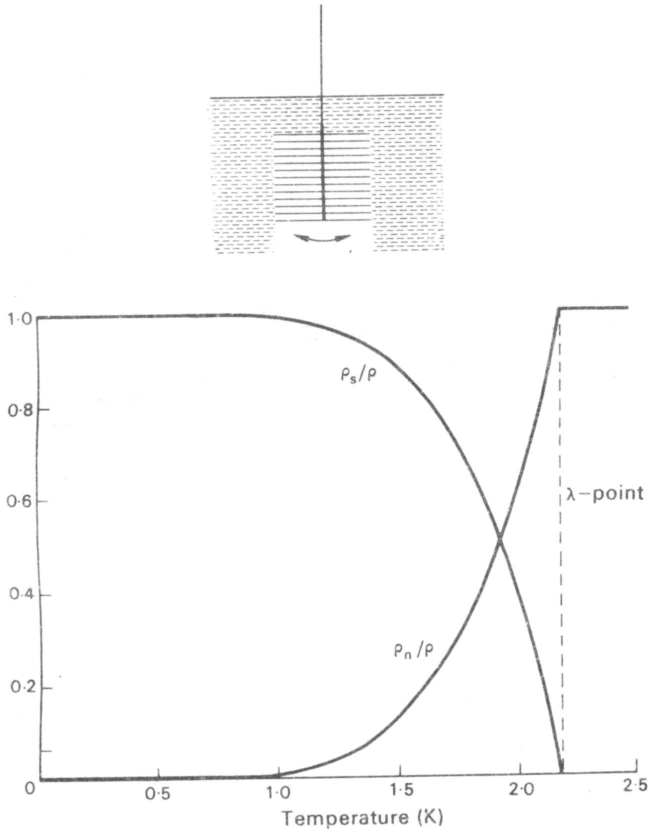

FIG. 1.7 Andronikashvili's experiment (after Atkins 1959).

Another example of the flow properties of liquid He^4 below the λ-point is provided by the *film* which covers the exposed surface of a body partially immersed in He II. Adsorption on a surface in contact with any liquid or its saturated vapour is common enough, but He II films are unusually thick. Optical measurements (Jackson and Grimes, 1958) revealed that a typical thickness under saturated vapour is 30 nm or about 100 atomic layers, sufficiently wide to permit superfluid flow through the film. Owing to the presence of the film on its walls, an empty beaker lowered into a He II bath begins to fill with bulk liquid, even though the rim is kept well above the bath surface (Fig. 1.8). Filling continues until the inner level reaches the level of the bath, at which point it stops. If the beaker is now raised, it empties itself again, and if it is raised clear of the bath, drops are seen to fall from the base of the beaker. We conclude that the superfluid fraction flows through the film whenever there is a height difference between the two bulk liquid levels. In other words, the film acts like a siphon, the driving force for the superfluid being provided by the gravitational potential difference between the

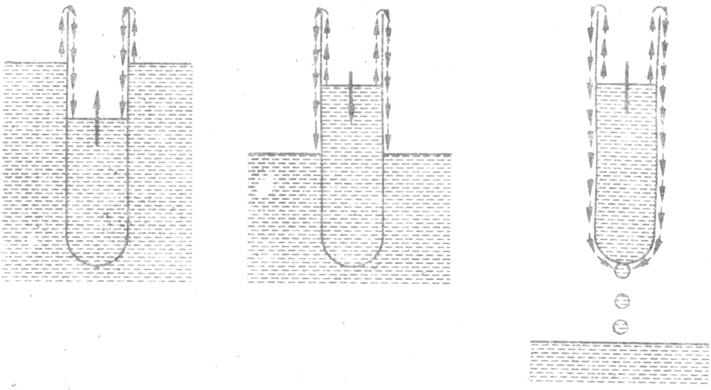

FIG. 1.8 Film flow of He II over the walls of a beaker.

ends of the film. By observing the rate at which the beaker liquid level changes, the superfluid velocity may be determined; a typical value is 20 cm s^{-1}. On the other hand, by virtue of its viscosity, the normal fluid fraction is almost stationary in the film. We shall discuss film flow in greater detail in Chapter 2.

Early experiments designed to measure the *thermal conductivity* of He II showed that it is very high, tending to infinity for small heat currents. In fact it is impossible to establish a temperature gradient in the bulk liquid, a result which explains the sudden cessation of boiling as the liquid is cooled through T_λ. In ordinary liquids, a bubble is formed when the local temperature is sufficiently greater than that at the free surface. In He II, supposing that a large enough temperature fluctuation were to occur, it would decay so quickly that a bubble would not appear. Thus evaporation of He II takes place only at the free surface.

A temperature gradient can be set up between two volumes of bulk He II provided that they are connected only by a superleak, that is a channel through which the superfluid can flow, but not the normal fluid. A common form of superleak is a tube packed tightly with fine powder: the spaces between the particles form winding channels of varying width (typically ~100 nm) which allow the superfluid to pass and clamp the normal fluid. If heat is supplied to one side of the superleak, a pressure head is set up as well as a temperature difference (Fig. 1.9). This happens because the superfluid fraction flows from the low-temperature side to the high-temperature side of the superleak. Since ρ_s/ρ increases with decreasing temperature, we infer that the superfluid moves to the region of higher temperature in order to reduce the temperature gradient.

A dramatic demonstration of this effect is furnished by the so-called *helium fountain*, first seen by Allen and Jones (1938) (Fig. 1.10). The superleak in this case is a wide tube containing emery powder. One end is open to the He II bath, while the other is joined to a vertical capillary. When the emery powder is heated, the superfluid flows into the superleak with such speed that He II is forced out of the

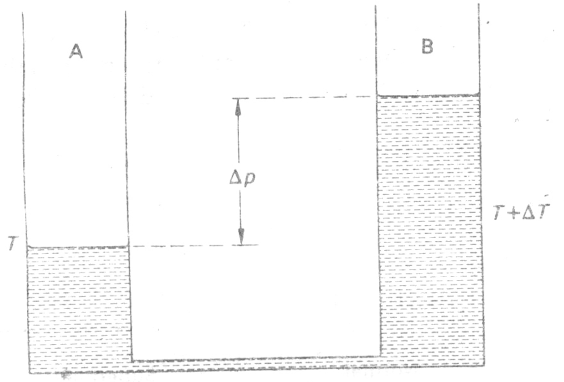

FIG. 1.9 Two vessels connected by a superleak. A temperature difference between the two is accompanied by a pressure head.

capillary tube in a jet. The heat provided by a small hand torch is sufficient to produce a fountain rising to heights of 30 or 40 cm.

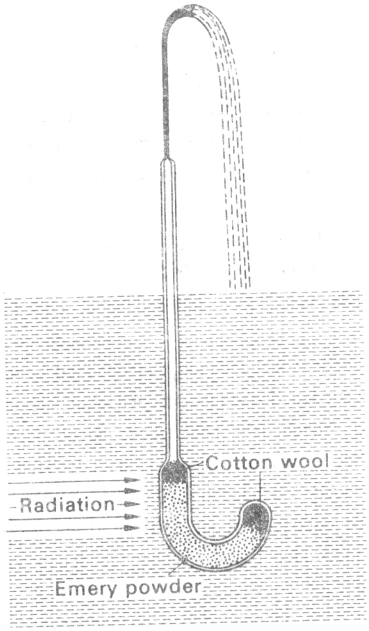

FIG. 1.10 The helium fountain (Wilks 1967, after Allen and Jones 1938).

These manifestations of the *thermomechanical effect* show clearly that heat transfer and mass transfer in He II are inseparable. The steady supply of heat to the bulk liquid, achieved for example by passing direct current through a resistor, and its removal elsewhere into a constant-temperature reservoir causes internal convection (Fig. 1.11). Normal fluid flows from the source to the sink of heat, whilst superfluid flows in the opposite direction, under the constraint that the total density remains constant everywhere. Thus heat is not transferred in He II by the ordinary processes of conduction and simple convection of the whole fluid. Only the normal fluid fraction carries heat; superfluid flow by itself cannot transport heat.

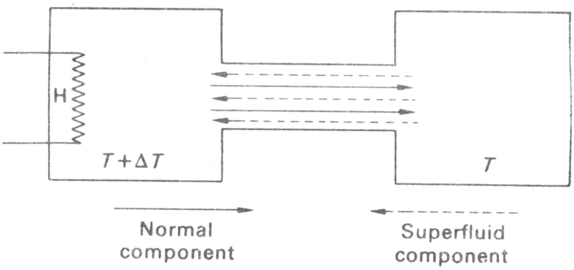

FIG. 1.11 Internal convection in He II. Heat is supplied by heater H and temperatures are held constant.

When the heat supply to He II is made to vary periodically, by passing alternating current through the resistor, the two fluids oscillate in antiphase with one another. Once more, this has no effect on the total density ρ which remains uniform throughout. The result is that the local value of the ratio ρ_s/ρ, and consequently the local temperature, undergo oscillations. In this way He II is able to propagate temperature waves, which are given the name *second sound* to distinguish them from *first sound*, the ordinary longitudinal pressure waves involving fluctuations in the total density at constant temperature. Provided that the rate of heat supply is not too large, and the frequency not too high, second-sound waves are propagated with virtually no attenuation. We shall discuss second sound in more detail after we have introduced the two-fluid hydrodynamic equations in Chapter 2.

The behaviour of He II when set into rotation can be described in terms of the two-fluid model, but this is a much more complicated situation than the properties we have described so far, and, for instance, it is not possible to ignore the interaction between the two components. In a rotating vessel, the normal fluid behaves in the expected way, undergoing *solid-body rotation*. The superfluid fraction appears to do the same, but in reality it experiences vortex motion. A series of vortex lines threads the fluid in the rotating vessel. Superfluid rotates round each line, the angular momentum associated with each vortex being quantized. The occurrence of vortices in the superfluid is not limited to the case of a rotating vessel; indeed it is extremely easy for vortices to be created in many situations involving superflow. Vortices in liquid helium will be discussed fully in Chapter 4.

To conclude this introductory section, we turn our attention to the entropy of He II. Looking again at the phase diagram for He^4 (Fig. 1.1), we see that the melting curve is steep for $T > T_\lambda$, but that it changes its slope rapidly below T_λ, eventually becoming horizontal as $T \to 0$. The gradient of the melting curve is determined by the appropriate Clausius–Clapeyron equation:

$$\frac{\mathrm{d}p_{\mathrm{m}}}{\mathrm{d}T}=\frac{\Sigma_{\mathrm{liq}}-\Sigma_{\mathrm{sol}}}{V_{\mathrm{liq}}-V_{\mathrm{sol}}}=\frac{\Delta\Sigma_{\mathrm{m}}}{\Delta V_{\mathrm{m}}} \tag{1.3}$$

where Σ is entropy and V is volume, and the subscripts have obvious meanings. Above the λ-point $\Delta\Sigma_{\mathrm{m}}$ is large, but immediately below T_λ it decreases quickly to become virtually zero for all temperatures below 1 K. In this range, therefore, the liquid cannot lose entropy by solidifying, and the liquid phase is the stable one when the temperature is very close to zero. We conclude that $\Sigma_{\mathrm{liq}}\to 0$ as $T\to 0$, in agreement with the Third Law of Thermodynamics. In view of the experimental evidence that also $\rho_s/\rho\to 1$ as $T\to 0$, we conclude that at absolute zero He II is entirely superfluid and possesses zero entropy. In consequence, it is logical to assume that at finite temperatures the superfluid fraction carries no entropy. Indeed, this is an alternative way of saying that the superfluid can flow without dissipation, since any dissipative process invariably involves entropy production. Thus the entropy of He II is confined to the normal fluid, as might be expected after discussing internal convection, in which the normal fluid is responsible for the transport of heat.

It is clear that the pure superfluid constitutes the ground state of He II. The He^4 atom has a resultant spin of zero, and is therefore a boson; an assembly of He^4 atoms is governed by Bose–Einstein statistics. As is well known, an ideal boson gas of particles with non-zero rest mass exhibits the phenomenon known as the *Bose–Einstein condensation.* At low temperatures, the particles tend to crowd in to the same quantum state, the lowest single-particle energy level of the system, forming a *condensate.* The condensation begins at a certain critical temperature and is complete at absolute zero. It seems certain that liquid He^4 behaves in a very similar way. The λ-point is the temperature which marks the onset of condensation, and the condensate is associated with the superfluid fraction of He II. We shall discuss the Bose–Einstein condensation in § 1.3. Before that, in § 1.2, we introduce the basic properties of superconductors, and then later on in the chapter we shall describe how the idea of a condensate can be applied to both superfluid helium and superconductors.

1.2 Basic properties of superconductors

Superconductivity is a phenomenon with many features in common with the superflow of He II. One immediate difference is that there are many metals which become superconducting at a sufficiently low temperature, whereas superflow in a liquid is unique to He II. The simplest property of the superconducting state is that it is one in which an electric current, if it is small enough, can flow without a voltage appearing; this is analogous to the superflow of He II through a thin channel or a surface film. Superconductivity is characterized by a critical temperature T_c; the resistance of a superconducting wire drops to zero more or less discontinuously at T_c. It is believed that the superconducting state really is a state of zero resistance, and not simply a state of very low resistance. An elegant way of demonstrating that the currents do flow without resistance is to suspend a bar magnet above a concave superconducting dish. The induced supercurrents act to repel the magnet, and it stays suspended indefinitely. Shoenberg's book (1952) contains a photograph of this experiment, which of course resembles the persistent superflow of He II in a torus.

The transition to superconductivity is a virtually perfect second-order phase transition; that is, there is no latent heat, and a sharp finite discontinuity in the specific heat. Figure 1.12 shows the specific heat as a function of temperature for Nb, which is typical. This almost ideal behaviour of the specific heat in supercon-

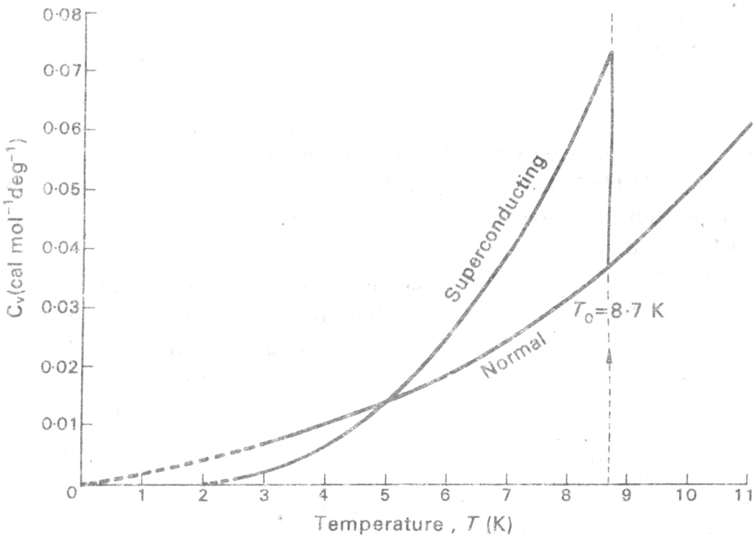

FIG. 1.12 Specific heat of Nb. Normal state values are measured in a magnetic field greater than H_{cb}. (After Brown *et al.*, 1953.)

ductors contrasts with the λ anomaly in helium (Fig. 1.4). We shall see in Chapter 4 that both the superfluid and superconducting states are characterized by a range of coherence ξ, which however is much shorter in He II than in superconductors; the behaviour of the specific heat is governed by the coherence range, in a way that we shall discuss in § 6.9.

Because so many materials undergo a transition to superconductivity, any discussion of the subject is inevitably complicated to some extent by the need to differentiate the behaviour of different classes of superconductors. The most complete tabulation of properties of superconducting materials is that given by Roberts (1971). Table 1.1, taken from that source, shows the elements which become superconducting with a critical temperature above 0·8 K. It can be seen that there is no simple rule to decide which elements become superconductors. However, the following points deserve mention. Firstly, only metals become superconductors. Secondly, all the critical temperatures are under 10 K; actually Table 1.1 does not include the highest critical temperatures, as some metallic compounds have critical temperatures of about 20 K. Thirdly, some metals which are good conductors at room temperature, notably the noble metals, do not