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MELTING AND SOLIDIFICATION OF HELIUM IN RESTRICTED GEOMETRIES

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Résumé.- Les processus de fusion et de solidification sont déterminés par les conditions microscopiques à l'interface liquide-solide. Des calculs théoriques et certaines observations optiques directes suggèrent que l'interface dans le cas de l'hélium a une épaisseur de plusieurs couches atomiques. Dans nos propres expériences sur la solidification de $^3$He à basse température ($\lesssim 100$ mK) dans une géométrie restreinte (verre poreux de type Vycor présentant des trous de diamètre $\sim 70\,\text{Å}$), nous avons utilisé le processus de solidification adiabatique qui crée le refroidissement de $^3$He (effet Pomeranchuk) pour la mesure des changements d'entropie et de volume en fonction de la pression et de la température à $2/3$ bar à l'intérieur de la couche de fusion. Nous avons aussi effectué des mesures d'aimantation. Les observations montrent que la géométrie restreinte fournie par le substrat de verre solide à grande surface peut avoir un effet important : en particulier ce processus de solidification adiabatique qui, bien que désordonné, est probablement mobile. Une telle situation pourrait aussi représenter une interface entre l'hélium liquide dans le récipient et l'hélium solide et nous comparons nos mesures avec d'autres qui donnent des indications indirectes sur la nature de cette interface.

Abstract. - The processes of melting and solidification are determined by microscopic conditions at the solid-liquid interface. Theoretical calculations and some direct optical observations suggest that the interface for helium is several atomic layers thick. In our own experiments on the solidification of $^3$He at low temperatures ($\lesssim 100$ mK) within a restricted geometry (Vycor porous glass with pore diameter $\sim 70\,\text{Å}$), we have made use of the adiabatic solidification process for cooling $^3$He itself (Pomeranchuk effect) to make measurements of entropy and volume changes as a function of pressure and temperature within $2/3$ bar of the melting curve. Measurements of magnetisation have also been made. The observations show that the restricted geometry provided by the high surface-area solid glass substrate can have a profound effect: in particular, it induces a high density ($\rho > \text{solid}$), high entropy phase which, although disordered, is probably mobile. Such a situation may also be representative of the interface between bulk liquid and solid helium, and we compare our measurements with others which give indirect evidence of the nature of this interface.

The efficiency with which highly polarized liquid $^3$He can be produced by melting of the solid depends on the nature of the melting interface, and in particular on the possible relaxation processes for nuclear magnetism within that interface. In this paper we briefly review the current understanding of the freezing and melting interfaces of classical solids, and consider the modifications to these ideas necessary when they are applied to quantum solids at low temperature. We then discuss various experiments which give information on the nature of the solid-liquid interfaces of $^3$He and $^4$He before showing that recent experimental work on the freezing of $^3$He and $^4$He in restricted geometries may be relevant to this problem. Finally we suggest that it is likely that relatively rapid relaxation of the nuclear spin system in high magnetic fields occurs at the melting interface of $^3$He.

A large body of knowledge exists from studies by varied techniques on the growth of pure crystalline solids from the liquid phase/1/. A consistent picture has been evolved in which the two experimentally observed forms of growth - faceting with plane surfaces corresponding to close packed atomic planes, and rounded surfaces of constant temperature - are understood as low and high temperature growth forms separated by a co-operative transition in the interface structure.

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Below a temperature at which the characteristic thermal energies are a fraction (close to unity) of the internal energy difference between the solid and liquid phases, low index close packed surfaces of the solid are atomically smooth, abruptly changing into the bulk liquid phase. Above the characteristic temperature the surface melts and undergoes a roughening transition, changing from an atomically smooth and abrupt interface to a diffuse one in which the fraction of atoms on lattice sites falls to zero over several atomic layers. These surfaces have no long range order and can accommodate themselves to any equilibrium shape which has a curvature that is always small on an atomic scale.

The two different surface types have different behaviours when freezing occurs. Atomically smooth surfaces are believed to grow by the progress of atomic steps across the surface, and because the binding of atoms to these steps is weaker than to a completed surface plane, substantial undercooling may be required to produce solid growth, whereas the roughened surfaces represent an equilibrium between the two phases and are believed to grow without undercooling. In equilibrium the form of the solid will be governed by the different surface energies of various atomic planes; in general, even below the roughening transition temperature the solid will show some rounding at the edges at which facets intersect, since these edges are more easily melted than a whole surface. In melting the difference in the form of the solid between the two surface types is much reduced; below the roughening temperature the high index surfaces melt more rapidly than the close packed smooth surfaces which they consume, giving a rounded appearance to the crystal. These high index surfaces are imagined to be composed of a series of randomly spaced ledges of lower index surface, with many kinks along the length of any step; although these melting surfaces are not ordered they are still believed to be relatively abrupt transitions between liquid and solid phases.

The stability of the liquid phases of $^3$He and $^4$He down to absolute zero is an immediate indication that, in addition to the thermal motion of the atoms, quantum mechanical zero point motion must be considered when the helium liquid-solid interface is modelled. There are three possible approaches: we can attempt to describe the zero point motion by an equivalent temperature and compare this with the roughening temperature; secondly, we can construct a quantum mechanical model of a roughened surface, for instance by considering quantum surface defect waves, and compare the energy with that of an abrupt interface; finally we can search for a new description of a quantum interface.

In view of the large amount of work on the possibility of ground state vacancies in solid helium /2/, it is natural to consider the extension of this work to surface vacancies. Guyer raised the possibility that inhomogeneous regions in helium might reduce their ground state energy by introducing vacancies which were restricted to that region /3/. A second approach has been taken by Andreev and Parshin who have considered a quantised version of the classic terrace-ledge-kink model /4,5/. In both these calculations the existence of mobile ground state defects depends on the width of the defect band compared with the excess energy associated with the formation of the defect. As has been the case of solid $^3$He, these authors argue that the bandwidth is such that the ground state includes a number of these surface defects.

Classical models of an interface treat the
liquid phase as a continuous medium, even on an atomic scale. This may be justified as the correlation time in the liquid is short compared with the thermal equilibrium time associated with bonding an atom onto a lattice site with the release of the appropriate binding energy. At the liquid-solid interface in helium this equilibrium time argument may no longer be valid since the energy release per atom will be small. In modelling the helium interface we need an atomic model of both liquid and solid phases, a version of which we will now put forward; this is similar in concept to that of Castaing and Nozières /6/.

The atomic description of solid helium is well established: the initial Hamiltonian is transformed by the use of single particle wave functions evaluated in a self-consistent fashion which "spread" the particle over the available volume, modifying the effective two-particle potential. This effective potential is then used to evaluate pair correlation functions between the "spread" particles, effectively keeping the hard cores of the particles apart. These two stages, which account for the dominant energies in a quantum solid, can be taken over to a cell model of liquid helium in which we spread the particles in a self-consistent fashion and then use pair correlation functions; such an approach should give the liquid structure factor. The difference between a liquid (or glass) and a solid in this model is in the number of nearest neighbours. In a perfect crystalline solid all atoms have identical numbers of nearest neighbours; this, together with a characteristic spacing, gives long range order. In a glass or liquid on the other hand the number of nearest neighbours fluctuates about an average: some atoms have an excess, corresponding to the presence of an interstitial atom, while others have fewer than the average, corresponding to a vacancy. An important distinction to be made at this point is that these vacancies and interstitials cannot be attributed to a particular site because the arrangement of atoms accommodates itself to the fluctuations in the number of nearest neighbours, giving rise to long range disorder. This distinction makes it difficult to proceed with the next step in developing this atomic picture of a liquid, namely changing the localised fluctuations in structure into delocalised "structural waves"; however we can make an important distinction between this description and that of vacancies in a solid with a lattice structure, namely the argument that a vacancy will favour a ferromagnetic $^3$He ground state /2/ is no longer obviously true, since the vacancies move in a structure that is disordered spatially as well as in its spin system.

Our motive for constructing this atomic cell model of a quantum fluid is to enable us to describe the solid-liquid interface, which we may now consider as an interface between a crystal and a quantum glass. At this stage we note that there are severe problems in using conventional models for the interface for helium; firstly these have been developed for solids with strong bonding, and hence, although the statistical physics of the theories suggests that the PAV term cancels in the equations, this term is always negligible in the examples which have been considered. Secondly the cause of the stability of the BCC crystal structure in $^3$He is poorly understood for it is not a close packed structure nor does helium have any directional bonding; because this structure is stable over a wider range of pressure at higher temperatures (both in $^3$He and $^4$He) we may surmise that the open nature of this lattice is also favoured by the zero point motion of the helium atoms. Since there is
neither close packing nor directional bonding it is difficult to justify applying a hill and valley picture of an interface which relies on the existence of a favoured site for each atom. The atomic cell model description of the liquid phase enables us to avoid some of these problems: as stated earlier the liquid phase includes both vacancies and interstitials; only the former may penetrate the surface layer of the crystal. This leads to a picture of an interface in which the number of nearest neighbours varies over a few atomic layers from that in the solid to that in the liquid by virtue of the penetration of vacancies a short distance into the crystal structure. These vacancies, localised at the surface, can be quantised to give excitations similar to Rayleigh waves; because they interact with the disordered liquid phase as well as the solid they may again no longer favour a ferromagnetic ground state.

The relaxation of the nuclear spin system in the interface depends on the correlation time of the local dipolar field and hence the frequency with which particles may interchange. The exchange interaction can be described in our model for the solid, the interface and the liquid. It comes from that part of one of the wave functions of adjacent atoms which overlaps on to that of the other. Since these have been constructed with the two body correlations built in, the direct overlap of the wave functions is small, and the principal contribution to the exchange interaction comes from interchange of the particles by pair rotation as in molecular hydrogen. From this argument it follows that the exchange interaction and hence the inverse correlation time varies continuously from the solid phase through the interfacial region to the liquid phase. This conclusion is similar to that of Castaing and Nozières that the relatively large susceptibility of the liquid compared with a Fermi system of that density is a consequence of it being nearly localized.

Experimental evidence relating to the nature of the liquid-solid interface in $^3$He at low temperatures is very limited. The most relevant results are those of two independent experiments on the rapid melting of polarized solid $^3$He /7,8/; in one of these there was evidence for an additional spin relaxation mechanism, possibly due to the nature of the liquid-solid interface. The other direct low temperature experimental information comes from the solidification of $^3$He in Pomeranchuk cells. Various features have been noted even in early experimental work /9/; in particular, while it is possible to supercool the liquid a small amount before any solid will nucleate, there is no evidence of any requirement for undercooling in order to continue the growth of existing regions of solid. In our own experiments with Pomeranchuk cooling we have seen similar thermal responses when stopping a compression or decompression while solid $^3$He is present, whereas, at least in the classical case, an abrupt interface would show a different response resulting from the differing surfaces present in melting and solidification. The success of Pomeranchuk cooling as a method of refrigerating both liquid and solid $^3$He also indicates that the irreversibilities associated with the growth of the solid, even down to 0.4 mK /10/, are very small. All this indirect evidence is consistent with the presence of an atomically rough interface between liquid and solid $^3$He at low temperatures.

Direct optical observations on the solid $^3$He - superfluid interface at temperatures down to 0.4 K have been reported recently /11, 12/. One feature of considerable interest is the apparent existence of a roughening transition of the surfaces perpendicular to the hexagonal axis at a temperature of
1.08 K. This transition is associated, according to the authors, with an instability in the interface against capillary waves of the variety suggested by Andreev and Parshin /4/. It is interesting to note that the surface tension does not have an observable temperature dependence above the roughening transition, and the roughened surface therefore has a low entropy. These observations present an example of the problem we face in describing the helium interface: in a classical system the interface would be abrupt below this roughening temperature, whereas Andreev and Parshin show that there may be quantum fluctuations at the plane of the interface corresponding to at least one layer in which the properties are intermediate between liquid and solid even below the roughening temperature. It may also be relevant to the nature of the $^4$He interface that the growth of B.C.C. $^3$He, which occurs above 1.4 K, never shows any faceting /11/; this might suggest that the extra amplitude of zero point motion in $^3$He could also be sufficient to eliminate faceting.

Another source of indirect information about the nature of the interface is experimental work on the nucleation of helium crystals on certain substrates. Lawson has shown that nucleation of HCP crystals of $^3$He with reproducible orientations can be induced by a single crystal gold surface with lattice dimensions commensurate with those of the desired atomic plane of $^3$He /13/. However these results are unusual, and most workers have found that, although nucleation may occur at the same point, the crystal axes have random variations between one experiment and another.

We have conducted experiments in which the entropy of $^3$He near a solid surface was measured as a function of pressure /14/. The surface in this work was provided by Vycor, a porous silica similar to a sponge in structure, with characteristic dimensions of about 70Å. This surface is presumed to be highly irregular on an atomic scale, but it provides a strong van der Waals attraction for the $^3$He atoms. A considerable amount of work has shown that the density of the $^3$He in the pores is enhanced, particularly so near the solid surface /15,14/. Thermal and magnetic studies have shown that at zero external pressure the $^3$He behaves as two weakly coupled systems, the layer adjacent to the surface having a $T^2$ specific heat and a Curie law susceptibility, while the remaining $^3$He behaves as a degenerate fermi liquid, but with a reduced fermi temperature, correlated with its higher density. /15/. In our experiments at around 40 mK we have found that there was no evidence for any marked change in the properties of this fluid part even when its average density exceeded that of solid $^3$He, until a pressure 0.7 bar below the bulk melting curve was reached. Between this pressure and about 0.2 bar below the melting curve a substantial amount of entropy was absorbed by the $^3$He in the Vycor, and its density also increased to a value considerably above that of bulk solid $^3$He. Magnetisation measurements showed only a small increase in susceptibility over this pressure range, although the failure to observe a larger increase may have been an experimental artefact. In related work in our laboratory using $^4$He, we have been unable to find any indication of solidification within porous Vycor up to, and indeed above, the bulk solidification pressure /16, 17/. A consistent picture of these results emerges if we interpret the high density phase found in the Vycor as one which is disordered and includes a large number of defects, as was suggested by Guyer /3/. These defects, which allow the dense phase to remain fluid, result in a similar atomic picture of the dense $^3$He in the Vycor.
to that of $^3$He at the solid-liquid interface. This possibility would be of major significance in the study of the interface of helium, since it is hard by other means to stabilise an area sufficient to produce significant experimental effects.

We now consider the nuclear spin relaxation processes at the liquid-solid interface of $^3$He using the model we have developed and the evidence from a small number of experiments. The longitudinal spin relaxation rate in $^3$He is proportional to the spectral density of the local dipole field at the Larmor frequency, $f_0$, and at $2f_0$. The total area of this function is equal to the RMS dipolar field which is constant; in most models of the form of this spectral density its value at frequencies greater than the inverse correlation time increases as the correlation time decreases, while for frequencies lower than this value the converse is true. It follows from this that the longitudinal relaxation time has a minimum value, for a fixed Larmor frequency, when the correlation time is close to the Larmor period. Since our description of the interface postulates a continuous variation in correlation time from the relatively large value in the solid to the small value in the liquid, it follows that there will be within the interface a layer in which the relaxation time is short even in large magnetic fields.

The importance of this layer in the melting process depends on its width, which in turn depends on the ability of vacancies to penetrate into solid $^3$He. This picture is consistent with measurements which were made on $^3$He in Vycor /14/: the spin-spin relaxation time did not change significantly in a field of about 250 gauss when the dense phase was being formed, implying that the correlation time in this phase remains short compared with both that in the localized layer adjacent to the surface and the Larmor period; this observation is consistent with this phase remaining fluid.

A possible indication of the distance over which enhanced relaxation might be observed comes from experiments by Giffard et al. on spin relaxation in solid $^3$He at higher densities /18/. In their experiments they observed that defect surfaces within the crystals provided an important relaxation mechanism whose effectiveness was difficult to account for. They interpreted these surfaces as small angle grain boundaries since they could be annealed at temperatures significantly below the solid melting temperature. In classical solids these grain boundaries are known to melt before the bulk crystal, and some have free energies comparable to twice the liquid-solid interfacial energy, and may be considered to include a liquid layer even significantly below the melting temperature. If this were to be the case in solid $^3$He, it would follow that these grain boundaries also allow experimental observations on the nature of the interface, and in particular the relaxation mechanisms associated with this interface. Hunt et al. reported low temperature relaxation times in samples of dimensions $\sim 0.1\text{ mm}$ and molar volume 24 cc ($J/2\pi = 25 \text{ MHz}$) of around 10 seconds /19/, which might be decreased by a factor of 4 in a field of 8T. As Castaing and Nozières have pointed out /16/, only a small region of the spin system near to the interface is out of equilibrium, but this is also the region in which the relaxation time is fastest. (The relaxation time appears to be proportional to the square of the distance from the relaxing surface.)

The experiments of Chapellier, Frossati and Rasmussen /8/ provide some confirmation that the relaxation in the interface is fastest in a region in which the effective exchange interaction is larger.
than in bulk solid. To polarise the solid $^3$He they started with liquid $^3$He in a Pomeranchuk cell in a high field and compressed to produce polarized $^3$He. If there was no relaxation at the interface this procedure would not work because the solid would be formed with its spin system out of equilibrium with both the lattice and liquid temperatures; however they were able to achieve polarizations of up to 20%, less than the polarization which would result from isotropic solidification, but nevertheless suggesting that relaxation occurs near the interface. Such a reduced polarization would be expected in our interface model in which the exchange interaction and relaxation time vary continuously in the region of the interface. The fastest relaxation rate will occur when the exchange and Zeeman interactions are comparable, equalising the temperatures of these two systems; because the exchange system has a larger heat capacity for a similar frequency it follows that the maximum polarization that can be produced by this method might be less than one half of the isentropic value.

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