

Absence of grain boundary melting in solid helium

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Received 16 August 2008, in final form 18 September 2008

Published

Online at stacks.iop.org/JPhysCM/20/000000

Abstract

Crystals are often expected to start melting at their free surface or at the interface between grains. Grain boundary melting corresponds to the situation where the interface between grains is invaded by a thick liquid film at the bulk melting temperature T_m . In some cases, premelting is predicted, with liquid-like layers appearing between grains at temperatures below T_m . We review this topic, and describe our experiments on solid helium 4. We find that grain boundaries are not wetted by the liquid at T_m : they emerge at the liquid–solid interface with a non-zero contact angle. This is consistent with a general argument which predicts that, although systems with short-range forces might show grain boundary melting and premelting, in systems with long-range forces (like helium), grain boundaries can only be wetted incompletely by the liquid at T_m .

1. Introduction

At the free surface of a crystal, the particles are in a state intermediate between the bulk solid and the bulk liquid. Therefore it seems reasonable to expect that the free surfaces will melt more easily. This explains why, usually, a crystal cannot be superheated, that is heated to a temperature above its bulk melting temperature T_m . This phenomenon, called surface melting, has been observed experimentally; for recent reviews, see [1–5]. What should we expect if the free surfaces are absent? This can be achieved by enclosing tightly the crystal in a box, or by heating only the centre of a crystal away from its boundaries. One may expect that *internal* surfaces, namely the grain boundaries in a polycrystal, may play a role: they could provide a favourable site for melting. The issue of GB melting has been a subject of debate and is reviewed briefly in [2, 4] and more extensively in [3, 6–9]. We show here how our observations on solid helium shed new light on the phenomenon. In section 2, we briefly review the theories related to this issue. We then describe the previous experiments in section 3 and our recent observations in section 4, and discuss their implications in section 5.

2. Theoretical predictions

The first accurate prediction of GB premelting was obtained by Kikuchi and Cahn [10] who studied a two-dimensional square lattice-gas model with particles interactions up to the

5th-nearest-neighbours. Using a mean-field approach, they calculated the density profile across a symmetric tilt boundary as a function of temperature at a constant chemical potential. They found that its width diverges near the bulk melting temperature. Besold and Mouritsen later confirmed these results using Monte Carlo simulations [11]: the calculated interfacial width as a function of the temperature offset from T_m could be fitted by a logarithmic divergence, as expected in mean-field theory.

Another interesting study is that of Broughton and Gilmer [12] on a three-dimensional system of particles interacting via a truncated Lennard-Jones potential. Using a harmonic analysis and molecular dynamics simulations, they found that sufficiently high angle GBs exhibit surface melting, and the disordered region between grains gradually expands as T_m is approached.

However, an argument due to Lipowsky [13] shows that a system with short-range interactions may exhibit GB premelting, but a system with long-range interactions cannot. Let us give here a slightly more detailed version. We introduce the operational definitions of σ_{GB}^0 , the surface energy between two grains *in direct contact*, and σ_{LS} , the liquid–solid surface energy. These quantities can be defined theoretically at other temperatures than T_m , and may depend on temperature. We define $\Delta\sigma^0(T) = 2\sigma_{LS}(T) - \sigma_{GB}^0(T)$. Let us consider a closed system at constant temperature T and pressure P . Let T_m be the bulk melting temperature at pressure P . The Gibbs free energy change per unit area when the system changes from two

(Ed: David)

Processing/JPCM/
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EPS Liquids Conference
2008

Printed 3/10/2008

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grains in direct contact to two grains separated by a liquid film of thickness l is:

$$\Delta G(l) = Ltl + \Delta\sigma^0 + V(l), \quad (1)$$

where L is the latent heat of fusion per unit volume of the liquid, $t = 1 - T/T_m$ is the reduced temperature, and $V(l)$ is a term accounting for the interaction between the two liquid–solid interfaces. The equilibrium film thickness $l_{eq}(t)$ is found by minimizing $\Delta G(l)$.

Let us first consider the case of short-range forces (decaying faster than exponentially, as is the case for the two systems studied in [10–12]). For the asymptotic behaviour of V at large l , we can take $V(l) \sim K \exp(-l/\xi)$, where ξ is the bulk liquid correlation length at T_m . The limit $V(l) \rightarrow -\Delta\sigma^0$ when $l \rightarrow 0$ is often used to determine the constant K , but this is biased because the above expression for $V(l)$ is only valid in the asymptotic limit. Nevertheless, if $K > 0$, the GB is completely wet by the liquid at T_m , and the GB premelts, with an equilibrium thickness l_{eq} that diverges logarithmically at T_m :

$$l_{eq}(t) = \xi \ln\left(\frac{K}{\xi L t}\right). \quad (2)$$

This equilibrium is stable if $\Delta G(l_{eq}) < 0$, otherwise it is metastable. To observe premelting, one thus also need:

$$\Delta\sigma^0(t) < -Lt\xi \left[1 + \ln\left(\frac{K}{\xi L t}\right)\right]. \quad (3)$$

This requires $\Delta\sigma^0$ to be negative. This is expected, since in the limit of a vanishing mismatch between the two grains, the GB should not premelt nor even be completely wet at T_m ; this is well described by the above model, because then σ_{GB}^0 becomes small compared to σ_{LS} and $\Delta\sigma^0 > 0$. For instance, Broughton and Gilmer extended their approach of [12] to a series of mismatch angles ϕ [14], and predicted that ‘interfacial melting should occur for $\phi > 15^\circ$ ’. Equation (3) also gives the temperature interval in which premelting occurs. Finally, we note that if the GB is invaded by a macroscopic liquid layer, the *effective* surface energy between the two grains is $\sigma_{GB} = 2\sigma_{LS}$, satisfying Antonow’s rule.

On the other hand, if the particles interact via (long-range) van der Waals forces, $V(l) \sim -W/l^n$ for large l , with $n = 2$ and 3 for non-retarded and retarded forces, respectively. In a continuum description, Lipowsky explains that the Hamaker constant $12\pi W$ is ‘always positive for a liquid film intruding between two crystals which differ in their orientation but not in their density’, which corresponds to an attraction between the two liquid–solid interfaces. This arises from the definition of W in terms of the frequency-dependent dielectric functions of the different regions involved [15]. This tends to decrease the equilibrium thickness l_{eq} , even at T_m . Instead of vanishing completely, because of short-range repulsions or interfacial fluctuations, l_{eq} can remain finite, but microscopic. The GB can only be wet incompletely by the liquid at T_m , and $\sigma_{GB} = 2\sigma_{LS} + V(l_{eq}) < 2\sigma_{LS}$.

Finally, we mention another interesting possibility: using a $Z(N)$ model (with short-range interactions), Schick and Shih [15] found that, instead of being wet by the liquid, the GB

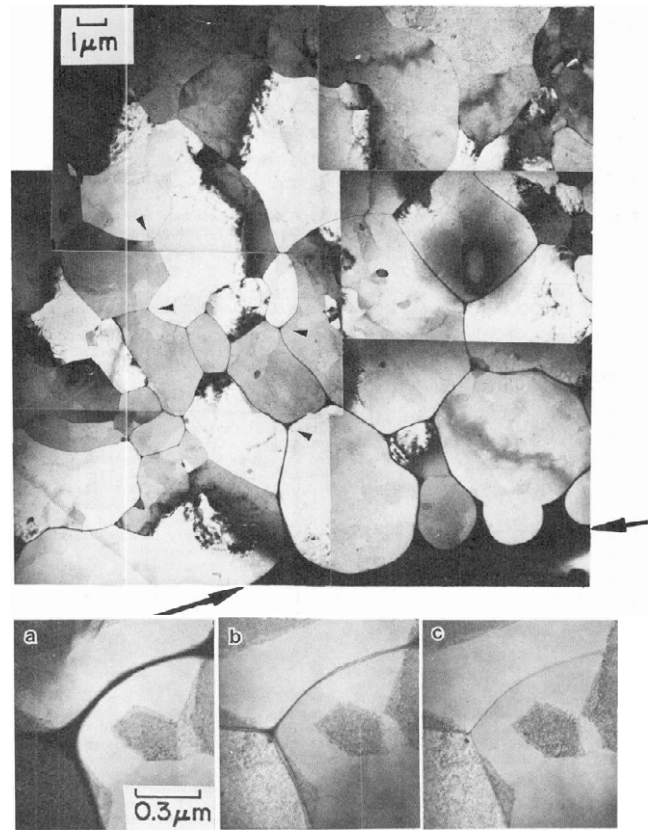


Figure 1. 400 nm thick aluminium films observed by transmission electron microscopy [17, 18]. Upper panel: the film is melted in a temperature gradient, and the liquid–solid interface appears at the bottom right corner (indicated by large arrows). In its vicinity, the grain boundaries and the vertices between three grains (indicated by small arrows) are invaded by the liquid. The thickness of the liquid layer decreases as one moves away from the liquid–solid interface (decreasing temperature), and eventually falls below the 0.7 nm resolution at a temperature estimated to be below T_m by less than 0.1%. Lower panel: disappearance of the liquid layers and of the liquid vertex between three grains when cooling (left to right) from very near T_m . Reprinted figures 5 and 6 with permission from [17]. Copyright 2007 by EDP Sciences.

could be wet by another grain with an intermediate orientation. They discussed how this behaviour would be modified in the case of long-range forces, and they proposed that a ‘thick, but finite solid layer’ could invade the GB.

3. Previous experiments

The first direct observation of GB melting was reported by Glicksman and Vold [16]. They studied 50–100 nm thick films of bismuth protected by carbon layers with transmission electron microscopy. When molten in a temperature gradient, the liquid–solid interface adopted a given position along the isotherm at T_m , close to which the grains in the film were detached from each other: the GBs and the vertices between three grains were invaded by the liquid.

Balluffi and Hsieh [17, 18] made similar observations on 400 nm thick aluminium films with hot stage transmission electron microscopy (figure 1). They noticed that the

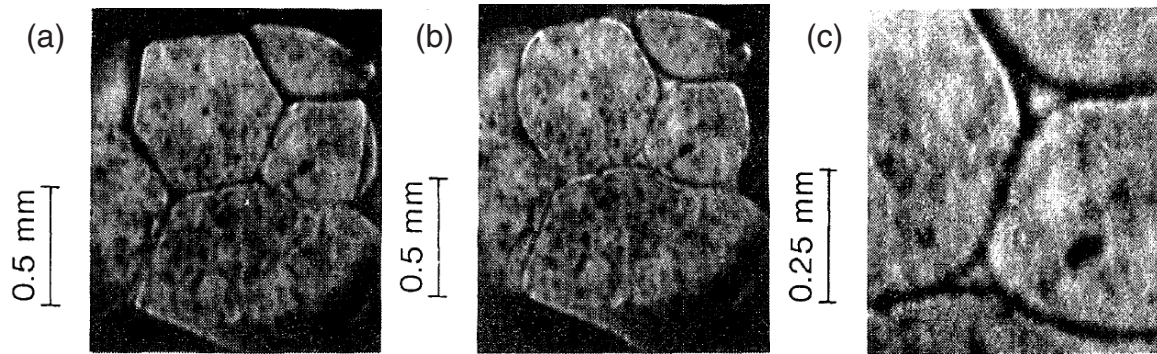


Figure 2. (a) fcc helium film (about $50 \mu\text{m}$ thick) observed by Franck *et al* [19, 20] on the basal plane of sapphire, at 280 MPa and 26.3 K. (b) Upon heating, the vertices between grains fill with liquid. (c) Enlarged view of two vertices, showing dihedral angles less than 30° . Reprinted figure 1 with permission from [19]. Copyright 1983 by the American Physical Society.

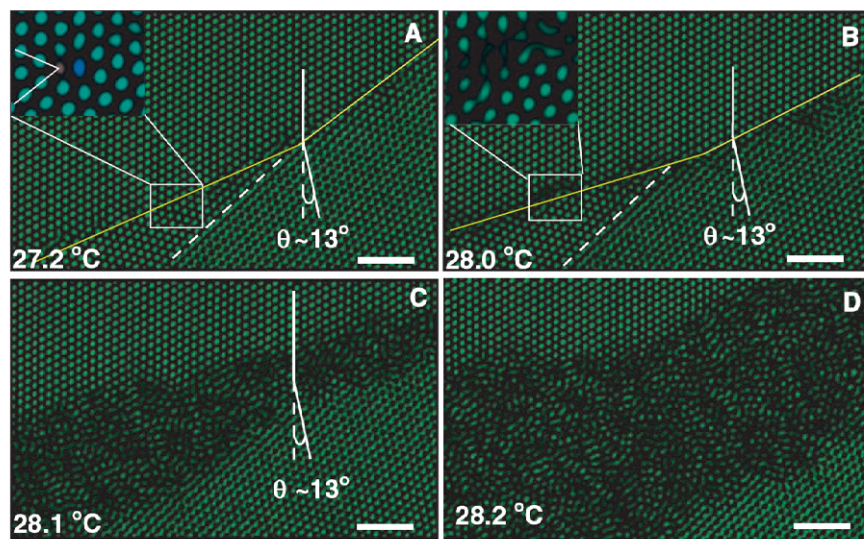


Figure 3. Premelting of a colloidal crystal at a grain boundary [23]: the temperature in pictures (A), (B), (C), and (D) is 27.2, 28.0, 28.1, and 28.2 °C, respectively. The melting temperature of the bulk crystal is 28.3 °C. From [23]. Reprinted with permission from AAAS.

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separation between grains decreased away from the T_m isotherm, until a distance was reached at which the grains appeared connected (the GB width became less than the 0.7 nm resolution). Using a conservative estimate of the temperature gradient, they concluded that ‘no complete grain boundary melting was detectable by local diffraction contrast at temperature lower than $0.999 T_m$ ’ [17, 18].

Franck *et al* [19, 20] studied solid helium films about $50 \mu\text{m}$ thick with a Schlieren method, at high temperature and above 50 MPa. For the fcc phase, a polygonal, foam-like structure was observed (figure 2(a)). The observations were similar to those for metallic films described above: upon heating, the vertices of the foam widened into a curved triangular shape, before melting occurred at the GBs, the grains of the crystal becoming separated. Measurement of the dihedral angle 2θ at a GB was difficult (figures 2(b) and (c)) and gave $0^\circ \leq 2\theta \leq 30^\circ$. In contrast, the hcp phase exhibited banded structures, with no GB melting, which suggested partial wetting of the GBs, although 2θ could not be

measured [20]. Because of the observations made on the fcc phase, this experiment is cited by Dash *et al* as an evidence for near complete wetting [21] or even premelting [22] of the GBs.

More recently, Alsayed *et al* [23] observed GB premelting in a colloidal system. It consists in charged microgel particles in a buffer solution; their radius is around 375 nm, and, most importantly, it depends on temperature because of water moving in and out of the microgel. Consequently, the volume fraction of the particles in the solution can be tuned, allowing the formation of a close packed crystal at low temperature and its melting at $T_m = 28.3^\circ\text{C}$. They observed that a small angle ($\approx 13^\circ$) GB (figure 3(A)) started to premelt at 28.0°C , at which the volume fraction is still higher than the one required for melting. The GB is invaded by a liquid-like layer (figure 3(B)) whose width increases as the temperature is raised to 28.2°C (figures 3(C) and (D)). One could say that premelting thus occurs within 0.1% of T_m , but the relevant parameter here is the volume fraction rather than the temperature, which renders it difficult to define a range of premelting.

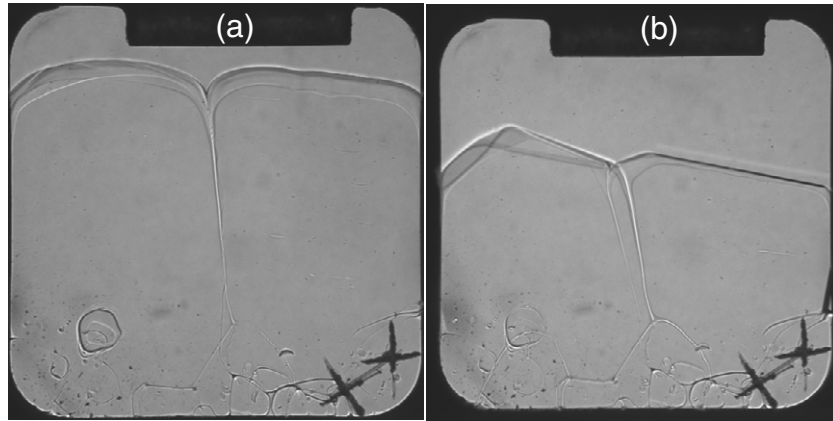


Figure 4. A GB makes a groove when emerging at the liquid–solid interface (a). The growth shapes (b) show that the two grains have a different orientation. The groove dihedral angle 2θ is not zero [25, 26], indicating the absence of complete wetting of the GB by the liquid. The bright lines near the vertical correspond to the liquid channels created by the GB on each glass windows of the cell. Their width is a few tens of micrometres: it depends on the depth below the top of the liquid–solid interface. Other pictures are displayed in [25].

4. Observation of grain boundaries in helium 4

Helium has no triple point. It can thus be observed in the liquid phase at temperature approaching the absolute zero. The liquid becomes superfluid below around 2 K, and solid above $P_m = 2.53$ MPa near 0 K. Very high quality single crystals can be grown from the superfluid. Helium crystals have been studied extensively: for more details, see the recent review given in [24].

In this section we describe our recent measurements of the wetting properties of GBs between helium crystals at low temperature (50 mK) [25]. For a detailed description of the experimental setup and procedure, we refer the reader to [26]. In short, we use an optical dilution cryostat to look at crystals grown in a square cell whose dimensions are 11 mm \times 11 mm \times 3 mm. The small thickness of 3 mm is chosen so that the GBs lie in planes oriented nearly perpendicular to the two windows, that is parallel to the optical axis. At the same time, 3 mm is large enough compared to the capillary length $l_c = \sqrt{\sigma_{LS}/[(\rho_S - \rho_L)g]} \simeq 1$ mm to reduce the effect of the windows on the groove shape. Results in a thicker cell (10 mm) are qualitatively similar, but the grooves are not perpendicular to the windows, making quantitative measurements difficult. We shine parallel white light through the sample and take images with a CCD camera. Both liquid and solid are transparent, but they have a small difference in refractive index that makes the interface visible. To prepare a GB, we use the following procedure: we first fill the cell with liquid at a pressure near freezing; we then inject mass sufficiently rapidly to avoid closing the fill line with a solid plug, and we obtain a cell full of a solid sample with many grains; we then melt the sample slowly until we keep only two grains which can finally be grown slowly to fill the lower part of the cell and exhibit a nearly vertical GB in the middle. An example of the bicrystal obtained is shown on figure 4(a). In this case, some smaller grains were left at the bottom of the cell; this does not affect the results: see [25, 26] for other examples, with only two grains and a GB closer to the vertical. When the crystals grow at low temperature, they exhibit facets

that reveal the difference in orientation (figure 4(b)). Two main features appear in figure 4(a): the groove at the liquid–solid interface and the two roughly vertical bright lines. The groove is created by the GB when emerging at the liquid–solid interface in order to satisfy the Young–Laplace equation, insuring mechanical equilibrium between the three interfaces involved:

$$\sigma_{GB} = \sigma_1 \cos \theta_1 + \sigma_2 \cos \theta_2, \quad (4)$$

where σ_{GB} , σ_1 and σ_2 are the interfacial tensions between the two grains, the liquid and left grain, and the liquid and right grain, respectively, θ_1 and θ_2 are the angles measured near the groove between the liquid–solid interface and the extrapolation of the GB plane into the liquid; the dihedral angle is then defined as $2\theta = \theta_1 + \theta_2$. Photographs such as the one displayed on figure 4(a) show that θ is not zero, that is that the GB is not wet by the liquid, even at the liquid–solid equilibrium. To measure θ , we fitted the interface profiles near the bottom of the groove with a one-dimensional Laplace equation [26]. We obtained $\theta = 11^\circ \pm 3^\circ$, $16^\circ \pm 3^\circ$, and $14.5^\circ \pm 4^\circ$ for three different samples. The dihedral angle may vary from one sample to another, because of the various misorientation between the two grains. The error bars are calculated from the fitting procedure: the uncertainty on the interface position (one pixel of the CCD) converts into an uncertainty in the fitting parameters of the Laplace equation.

The absence of complete wetting is consistent with the simulations by Pollet *et al* [28]. They found that the thickness of the disordered region between two grains was three atomic layers, whereas complete wetting requires a macroscopic thickness. In addition, they predict generic GBs to be superfluid, with a critical temperature in the range 0.2–1 K. This could be relevant to some aspects of the supersolid effects observed in solid helium 4; see [29] for a review.

We now turn to the roughly vertical bright lines on figure 4. They correspond to liquid channels opening on the windows (figure 5), because of the interfacial energy gained by replacing some solid on the window by the liquid. We have used a simple capillary model to account for this [25–27]: the

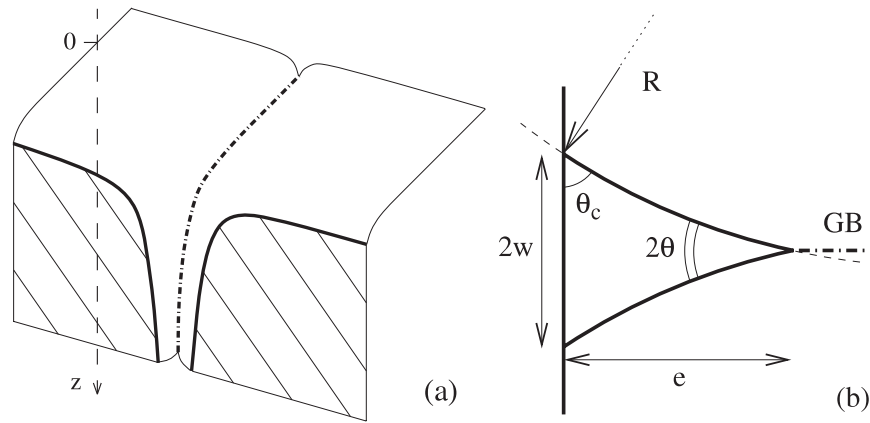


Figure 5. (a) Three-dimensional view of the contact between a grain boundary (dash-dotted line) and a wall. The hatched area shows the contact of the wall with the solid. (b) Horizontal cross section of the liquid channel near the wall. Reprinted figure 3 with permission from [25]. Copyright 2007 by the American Physical Society.

channels have a triangular cross section (figure 5(b)), whose size is limited by the competition of the interfacial energy with the volume energy due to the hydrostatic head pressure at a distance z below the top of the grains, which favours the solid. The liquid at a pressure above P_m can be at equilibrium with the solid, if the interface is curved with the liquid on the convex side. This is possible if the contact angle θ_c of the liquid–solid interface on the window (figure 5(b)) satisfies $\theta + \theta_c < 90^\circ$. We have directly measured θ_c and we found around 45° [26], so that this condition is fulfilled for bicrystals like the one on figure 4. The capillary model was shown to quantitatively account for the inverse proportionality between the channel width w and the depth z , measured for five different samples [25–27]. Typically, $w = 20 \mu\text{m}$ at $z = 10 \text{ mm}$. We also predict that, except perhaps in the presence of inhomogeneous stresses, these channels should be of atomic size at about 3.5 MPa ($P_m + 1 \text{ MPa}$), and vanish above this pressure.

5. Discussion

The works reviewed here confirm the predictions by Lipowsky [13]. The systems that exhibit GB premelting correspond to short-range interactions, as in the simulations described in section 2, or in the colloidal system studied by Alsayed *et al* [23]. In the latter case, the charged beads interact via electrostatic forces, exponentially screened by the ions in solution. On the other hand, bulk helium crystals have GBs which are only partially wet by the liquid at T_m , as is expected for long-range interactions. We note that one can imagine systems where a high amplitude short-range force may compete with small amplitude long-range forces, resulting in a relatively thick liquid layer between two grains at T_m [30].

As for the experiments on films, we think that they should be reconsidered. The thin thicknesses involved, and the contact with a substrate, may well favour the intrusion of the liquid in the GB, even if it would not occur between two bulk grains. In particular, we have seen above that liquid channels may open at the intersection of a GB and a wall. Their size increases when

the temperature increases toward T_m , so that it could reach the film thickness and make the grains detach. It also explains why the contrast is lost when the temperature is lowered 50–100 mK below T_m in the experiment by Franck *et al* [20], and why the GBs remain dry far enough from the liquid–solid interface in the temperature gradient used in experiments with electron microscopy [16–18].

In addition, in classical systems, even if the materials used are of high purity, the GB can be covered by adsorbed or segregated impurities. In that case, a melting-point depression due to the impurities may occur. This points out another advantage of studying systems where impurities are absent, as colloidal systems or helium.

Carrying on the analysis of the capillary model presented above, we have predicted that stable liquid channels could also exist at the junctions between three grains at a pressure P above the melting pressure P_m [26]. If the dihedral angles of the 3 GB grooves involved are less than 60° , the volume energy cost of replacing the solid by the liquid can be overcome by the gain in surface energy when replacing interfaces between grains by liquid–solid interfaces. The details of the calculation and the dependence of channel size on $P - P_m$ can be found in [26]. In fact, this idea had already been proposed by Miller and Chadwick [31] and rediscovered by Raj [32]; in both cases, they considered a temperature departure from equilibrium, but this is equivalent. References [26, 29, 33] explain how the properties of such liquid channels in solid helium may be important in the context of supersolidity, especially for some of the mass flow experiments [34, 35]. Networks of liquid channels have been observed in ice, where they are called *veins* [36, 37]. The impurities present in ice cores retrieved from Greenland and Antarctica are often used as indicators of the past climate. As the veins allow a faster diffusion of impurities, it has been proposed that they could affect the validity of the climate reconstruction [38].

6. Conclusion

A consistent picture emerges from the analysis of the theoretical and experimental work reviewed here. The direct

visualization of the wetting properties of GBs is difficult, but it is possible in colloidal systems and helium crystals. These two systems exemplify two kinds of behaviour: the former, short-range system exhibits complete wetting and premelting of a GB, whereas the latter, long-range system shows that wetting of the GB is only partial, even at T_m . These observations are in line with the predictions by Lipowsky [13].

Acknowledgments

We thank Milton W Cole and Siegfried Dietrich for enlightening discussions. We are grateful to T-E Hsieh, K Kornelsen, and A Yodh for giving us permission to reproduce their figures. This work is supported by ANR grants 05-BLAN-0084-01 and BLAN07-1-215296.

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