RECEIVED
JUL 29 1997
OSTI

Science, October 1995

Fluctuations During Melting*

M. Grimsditch

Materials Science Division, Argonne National Laboratory, Argonne, IL 60439

and

V.G. Karpov

State Technical University, 195251 St. Petersburg, Russia

The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. W-31-109-ENG-38. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

SCIENCE

DISCLAIMER

jmc

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

* Work supported by the U.S. Department of Energy, BES-MS contract #W-31-109-ENG-38 and travel grant (#931647) from the North Atlantic Treaty Organization.

ng

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

FLUCTUATIONS DURING MELTING*

M. Grimsditch

*Materials Science Division
Argonne National Laboratory, Argonne, IL 60439*

and

V. Karpov

*State Technical University
95251 St. Petersburg, Russia*

ABSTRACT

Repetitive melting and recrystallization, of crystals in a solid-liquid mixture in quasi-equilibrium, is reported. The experiments were performed at constant volume and ambient temperature inside a diamond anvil cell. The results, which we believe are the first to show the importance of fluctuations during a first order phase transition, can be partially understood on the basis of a recent generalized theory of Ostwald ripening.

Although fluctuations are known to play a dominant role in second-order phase transitions their role in first-order transitions does not seem to have been addressed in the literature. Most likely this omission is related to the fact that the most common observations of first order transitions, e.g. melting at constant pressure, occur discontinuously and may involve considerable hysteresis; both these conditions make the observation of fluctuations at the transition extremely difficult or impossible.

Recently however, two articles¹⁻² dealing with the Ostwald ripening stage in a system undergoing diffusive decomposition, introduced the possibility of the existence of long-range fluctuations. These articles extended the standard approach³⁻⁶ by including an interaction (mediated by local concentration gradients) between nuclei, and found that a characteristic length scale exists over which large amplitude fluctuations will occur. Since the conclusions reached in these articles should apply to all first order phase transitions, they should also be observable during melting. For melting the concentration gradients responsible for the interparticle interaction are simply replaced by the temperature gradients produced by the latent heat of fusion of a melting or growing crystallite.

We recall that Ostwald ripening is the latest stage of a first-order phase transition in which large particles of a new phase (ice, in our case)) grow at the expense of small particles. During this process the relative amounts of both phases remains practically constant. Ostwald was the first to realize that such a process is essential in order to decrease the total interface area and thus the surface energy. In particular, the lowest energy state of a solid liquid mixture is a single crystal surrounded by liquid. Although not ??? true equilibrium, a system at the ripening stage can be considered in quasiequilibrium in the sense that the thermal conductivity (or diffusion) processes are much faster than the characteristic ripening time.

Our observations were made on a system of many crystals evolving towards a single-crystal state. To achieve the Ostwald ripening quasiequilibrium condition the solid-liquid mixture was kept at constant volume. The phenomena we have observed under these conditions not only confirm the notion of interparticle interactions predicted by the analyses of Refs. 1 and 2 which

lead to the correlated melting and growth of crystallites, but also exhibit fluctuations involving repetitive melting and recrystallization of certain portions of some crystals.

Our experiments were carried out using a diamond anvil cell (DAC).⁷ This device consists of two truncated pyramidal diamond anvils. Between the tips of the anvils a ≈ 60 micron thick steel foil is placed in which a small ≈ 400 micron hole has been drilled. The material to be investigated, water, argon or CCl_4 in our case, is placed in this hole and the diamonds squeezed together. The behavior of the material in the cell can then be observed under a microscope. In all the images to be shown here the dark circular outline corresponds to the ≈ 400 micron hole in the steel and the features within correspond to crystal-liquid interfaces.

The initial stage involves squeezing the material until solidification occurs. Then, by slowly backing off on the force on the diamonds, the elastically deformed steel allows the volume in the hole to be chosen so that solid and liquid are in equilibrium. These conditions yield an almost perfect "constant volume" experiment. After this point is reached the cell is no longer adjusted and it remains undisturbed for the duration of the experiment. The evolution of the material in the cell is then observed as a function of time: typical runs lasted 6 to 18 hours and were recorded on a video tape. In our experiments we attempted to choose a volume which would give us comparable amounts of solid and liquid.

We are now left with the formidable task of describing to the reader, with the aid of only a few figures, the time evolution of the system. During the first few minutes the system evolves quite rapidly. Typically there are hundreds of small crystallites visible just after melting has occurred. Many of these crystallites disappear while others grow: Qualitatively at least, the evolution is as would be expected in an Ostwald ripening situation. During these initial minutes the superimposed images of crystallites at different depths made it impossible to detect any correlated evolution of adjacent crystallites.

After about 5 to 15 minutes (depending on the fraction of solid to liquid) the number of crystallites is sufficiently reduced so that there is little superposition of crystals at various depths. It is then relatively easy to follow the evolution of each single crystal. There are two phenomena

we observe which are related to the fluctuations: the first is the correlated behavior predicted in Refs. 1 and 2, the second is more spectacular and involves unexpected melting and resolidification within a single crystal.

Figure 1 shows three pictures of the crystallites in the cell corresponding to times: 61.6, 63.1, and 64.7 minutes after the system had been allowed to evolve on its own. The evolution shows clearly how the crystallite on the left grows at the expense of the disappearance of neighboring ones. In hindsight this is not that surprising: the conditions of the experiment, e.g., a constant fraction of solid and liquid, require that melting (solidification) in one portion of the cell must be accompanied by solidification (melting) elsewhere. This can be understood in a more quantitative manner in the formalism developed in Refs. 1 and 2.

Since Ostwald ripening in both diffusive decomposition and melting can be cast in an identical formalism, here we restrict ourselves to rewriting the results of Refs. 1 and 2 in terms of the parameters appropriate for melting. The critical radius is given by

$$a_c = \sigma / (T_\infty - T) \quad \text{with} \quad \sigma = (2 \alpha \Delta V T_\infty) / q \quad (1)$$

where T_∞ is the melting temperature at a flat interface, T is the average temperature, α is the surface energy, ΔV is the change in the volume per molecule in the two phases, and q is the latent heat per molecule. A particle of radius $a > a_c$ grows, while that of $a < a_c$ decays. In accordance with the results of Refs. 1 and 2 the fluctuations possess a characteristic amplitude $dT = T_\infty - T$ and length scale $L = 1/na^2$ (where n is the number of crystallites per unit volume and a is the average crystallite radius). The characteristic coarsening time is

$$\tau = (a/V)^3 (q/\sigma\chi) \quad (2)$$

where V is the volume per molecule and χ the thermal conductivity. By identifying a_c with the smallest crystallite size observed in our experiments (immediately after formation) which is typically 1 micron, and using other parameters typical for H_2O , we estimate that $L \approx 100\mu$, $\tau \approx 100$ sec, and $dT \approx 1^\circ C$. These estimates are consistent with the time scale of our observations and the distance between crystallites undergoing correlated evolution thus substantiating the theoretical description of Refs. 1 and 2.

The unexpected behavior exhibited by the system is shown in Fig. 2. The pictures have been chosen to highlight the transformations in the large crystal on the left. At 82 min the crystal is almost uniformly crystallized. At 91 min it has developed a melted region in the center which has partly melted through the crystal to the other side. At 94 min it has completely resolidified only to remelt at 97 min. The shape of the melted region changes shape dramatically from 97 to 112 min and finally it has almost completely recrystallized at 118 min. We emphasize that the duration of the fluctuations are many orders of magnitude longer than other characteristic times associated with the system; e.g. phonon transport over these dimensions are typically in the millisecond range.

Neither the conventional theory of Ostwald ripening nor the extensions of the theory given in Refs. 1 and 2 allow fluctuations of the type shown in Fig. 2. This shortcoming can be traced to the fact that the theory assumes that the concentration inside each nuclei is a predetermined constant. In the case of melting it is clear that this condition must be relaxed since there is no a priori reason why there should be no temperature gradients inside the crystals as well as in the liquid. We have not yet been able to find the general solution of multiple crystallites in quasi-equilibrium with liquid. The case of a single crystallite can however be solved and shows no possibility of melting within a crystallite.⁸ This finding is consistent with the experimental fact that, after evolving to one single crystal, our system no longer exhibits fluctuations. We interpret this as another indication that it is interparticle interaction which leads to the observed fluctuations.

Although the fluctuations highlighted in Fig. 2 and discussed above were the most spectacular we observed, other fluctuations of similar character were also observed. Two of the other crystals (the one in the center of the cell and the other just to its right) in Fig. 2 show the more usual behavior which is the melting in the middle of a crystallite. The melted region sometimes melts and resolidifies, sometimes it melts right through the sample, rarely it migrates to the crystal edge and vanishes into the liquid. We have also observed this type of behavior in CCl_4 and in Ar.

Another unusual fluctuation was observed in argon. In a load with only a few crystals, where the sizes had been changing very slowly and monotonically for almost an hour, suddenly, in a period of about a minute, one (and only one) of the crystals diminished in size to almost half its size and then grew back to close to its original size. Evolution then proceeded much as prior to the outburst.

At this point we are not able to provide a quantitative description of these local melted regions. Because the melted regions only appear during the time that the system is evolving with some crystallites disappearing and others growing, we believe that it is due to an intrinsic fluctuation of the liquid-solid and not due to some possible change in ambient temperature. Given the rather massive steel body of the DAC and the high thermal conductivity of the diamonds, it is also hard to imagine how a change in ambient temperature could produce local ($\approx$ tens of microns) hot spots within the cell. We believe that a more reasonable explanation is that the heat evolved as the external surfaces of a crystal solidify is somehow trapped in the solid and due to either geometrical factors or defected regions produces melting elsewhere. We cannot rule out of course that the diamonds themselves also play a role in redistributing the heat; however due to the very large thermal impedance between water and diamond this alternative seems unlikely to us.

In summary, we have observed dramatic fluctuations in melting and resolidification of liquids in equilibrium with their crystals at constant volume. These observations provide clear evidence for the existence for the recently predicted interparticle interaction during Ostwald

ripening. The magnitude and the nature of the fluctuations goes far beyond the scope of previous theoretical treatments and require further theoretical work for their explanation.

Work at ANL supported by U.S. Department of Energy, Basic Energy Sciences-Material Sciences under contract #W-31-109-ENG-38 and by a travel grant (#931647) from the North Atlantic Treaty Organization.

REFERENCES

1. V.G. Karpov and M. Grimsditch, Phys. Rev. B **51**, 8152 (1995).
2. V.G. Karpov, Phys. Rev. Lett. **74**, 3185 (1995).
3. I.M. Lifshitz and V.V. Slyozov, J. Phys. Chem. Solids **19**, 35 (1961).
4. C. Wagner, Z. Electrochemie **65**, 581 (1961).
5. P.W. Voorhees, J. Stat. Phys. **38**, 231 (1985).
6. V.V. Slyozov and V.V. Sagalovich, Usp. Fiz. Nauk. **151**, 67 (1987) [Sov. Phys. Usp., **30**, 23 (1987)].
7. A. Jayaraman, Reviews of Mod. Phys. **55**, 65 (1983).
8. R.L. Parker, Crystal Growth Mechanisms: Energetics, Kinetics and Transport, Solid State Phys., Vol. **26** (Academic Press, New York 1970).

FIGURE CAPTIONS

Fig. 1. Pictures of solid and liquid H₂O in a DAC at room temperature and roughly 1 Gpa. The three pictures were taken at 61.6, 63.1 and 64.7 minutes after the volume of the cell had been adjusted to give a reasonable fraction of liquid and solid and then left to evolve with no further external perturbation. The points to note are: the disappearance of the three small crystals in the top left, the concomitant growth of the large crystal on the left, and the almost static behavior of the rest of the crystals. To aid in the interpretation of the figure in the bottom picture we have labeled some of the solid (S) and liquid (L) regions.

Fig. 2. As in Figure 1 but at times 82, 91, 94, 97, 101, 105, 107, 112 and 118 minutes. The point to note is the melting and recrystallization of portions of the large crystal on the left as described in the text.

61.6 min.

63.1 min.

64.7 min.