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LETTER TO THE EDITOR

Fluctuations during melting

M Grimsditch† and V G Karpov‡

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

‡ State Technical University, 195251 St Petersburg, Russia and James Franck Institute, University of Chicago, 5640 S. Ellis Ave, Chicago, IL 60637

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Abstract. Fluctuations which involve the repetitive melting and recrystallization of crystals in equilibrium with their liquid are reported. The experiments were performed at constant volume and temperature inside a diamond anvil cell. The results, which we believe are the first to show the importance of temporal fluctuations during a first order phase transition, are not explained by any theory of Ostwald ripening.

The process by which a new phase appears during a first-order phase transition is often of nucleation and growth. It has been a common belief that the growth of particles is uniform in space so that the characteristic interparticle distance is the largest space scale in a system (provided the system is far from its critical point). Recently, however, two articles [1, 2] dealing with the Ostwald ripening stage in a system undergoing diffusive decomposition, introduced the possibility of the existence of long range fluctuations which span many interparticle distances and which have amplitudes of the order of the corresponding average values. These articles extended the standard approach [3–6] by explicitly including an interaction (mediated by local concentration gradients) between nuclei, and found that a length

$$L = \frac{a}{\sqrt{v}} = \frac{R}{v^{1/6}} \quad (1)$$

exists over which large amplitude fluctuations will occur. Here a and R are the characteristic nucleus radius and internuclear distance and $v = na^3$ is the second phase volume fraction. The origin of the fluctuations can be traced to the Coulomb nature of the diffusion field surrounding each particle; because the interparticle interaction has a long-range nature, many particles are needed to screen it.

Since the conclusions reached in [1, 2] should equally 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 freezing nucleus.

We recall that Ostwald ripening is the latest stage of a first-order phase transition during which large particles of a new phase (ice, in our case) grow at the expense of small particles. During this process the relative amount of the two 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 a true equilibrium, a system of many particles 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 testify in the favour of the prediction [1, 2] about correlated melting and growth and, more importantly, exhibit unexpected temporal 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 steel foil of thickness $\approx 60 \mu\text{m}$ is placed in which a small ($\approx 400 \mu\text{m}$) 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 behaviour 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 $\approx 400 \mu\text{m}$ 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 touched 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 6–18 hours and were recorded on a video tape.

We are now left with the formidable task of describing, with the aid of only a few figures, the time evolution of the system. During the first few minutes the system evolves quite rapidly. There are usually many ‘layers’ of 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 very large and superimposed images of the crystallites made it impossible to detect any correlated evolution of adjacent crystallites.

After about 5–15 min (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. After this point it is 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 behaviour predicted in [1, 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 of 61.6, 63.1 and 64.7 min after the system had been allowed to evolve on its own. The evolution shows clearly how the large crystallite on the left grows at the expense of the disappearance of neighbouring ones. This correlated evolution is not surprising because the conditions of the experiment, i.e. a constant fraction of solid and liquid, require that melting (solidification) in one portion of the cell must be accompanied by solidification (melting) elsewhere. What is surprising is that the particles that melt are not the smallest in the system as would be predicted by conventional Ostwald ripening theory. Although it does not prove it, this fact is indicative of the existence of a finite correlation radius. The order of magnitude of the ‘observed’ correlation radius (distance between growing and melting particles in figure 1) $L \approx 100 \mu\text{m}$ is consistent with the estimate given by equation (1).

Rewriting the results of [1, 2] in the terms of melting parameters we can also estimate

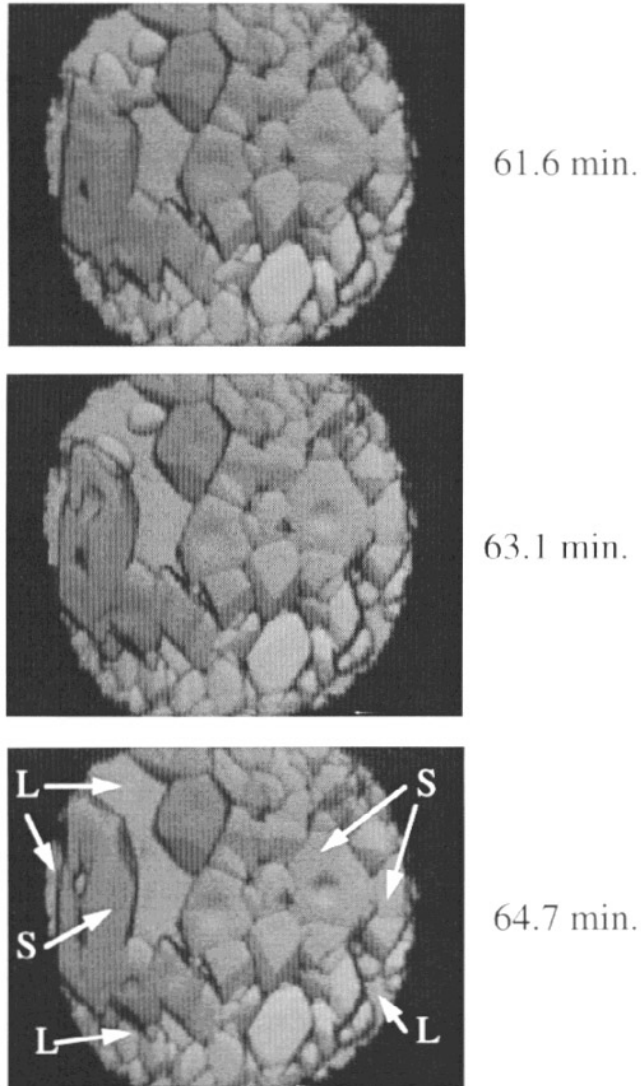


Figure 1. Pictures of solid and liquid H₂O in a DAC at room temperature and roughly 1 GPa. The three pictures were taken at 61.6, 63.1 and 64.7 min after the volume of the cell had been adjusted to give a reasonable fraction of liquid and solid and then left to evolve with no further external perturbation. 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 behaviour of the rest of the crystals. To aid interpretation, in the bottom picture we have labelled some of the solid (S) and liquid (L) regions.

other characteristic parameters of the system. The critical radius is given by

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

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 [1, 2] the fluctuations are expected to possess a characteristic amplitude $\delta T = T_\infty - T$. By identifying a_c with the smallest crystallite observed in our experiments and noting that immediately after formation we cannot resolve individual particles, we conclude that a_c is less than $1 \mu\text{m}$. Consequently $\delta T \gtrsim 1 \text{ K}$. The latter value is much larger than the characteristic thermodynamic fluctuation [8] $(\delta T)_t \sim T\sqrt{k/C} \sim T\sqrt{V/L^3} \sim 10^{-5} \text{ K}$, where C is the heat capacity and V is the volume per molecule. The characteristic coarsening time can be expressed as

$$t = \frac{a^3 q}{V \sigma \chi} \quad (3)$$

where χ is the thermal conductivity. Using parameters typical for H_2O we estimate $t \sim 100 \text{ s}$, which is consistent with the time scale of our observations. We again note that the arguments given above do not constitute a proof of the validity of the generalized theory of Ostwald ripening; they should only be taken as an indication that it might be valid.

The unexpected behaviour exhibited by the system is shown in figure 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 centre 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 is typically in the millisecond range. On the other hand the duration of the fluctuations is comparable to the coarsening time discussed above.

Although the fluctuations highlighted in figure 2 and discussed above were the most spectacular we observed, other fluctuations of similar character were also observed. The more common behaviour, melting in a circular portion in the centre of a crystallite, is shown by two other crystals (the one in the centre of the cell and the other just to its right) in figure 2. The melted region sometimes melts and resolidifies, sometimes it melts right through the sample, rarely the melted region migrates to the crystal edge and vanishes into the liquid. This type of behaviour we have also observed in CCl_4 and in Ar.

At this point we are not able to provide a quantitative description of the 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 room temperature could produce local (\sim tens of micrometres) 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.

Neither the conventional theory of Ostwald ripening nor the extensions of the theory given in [1, 2] allow fluctuations of the type shown in figure 2. This shortcoming can be partially 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

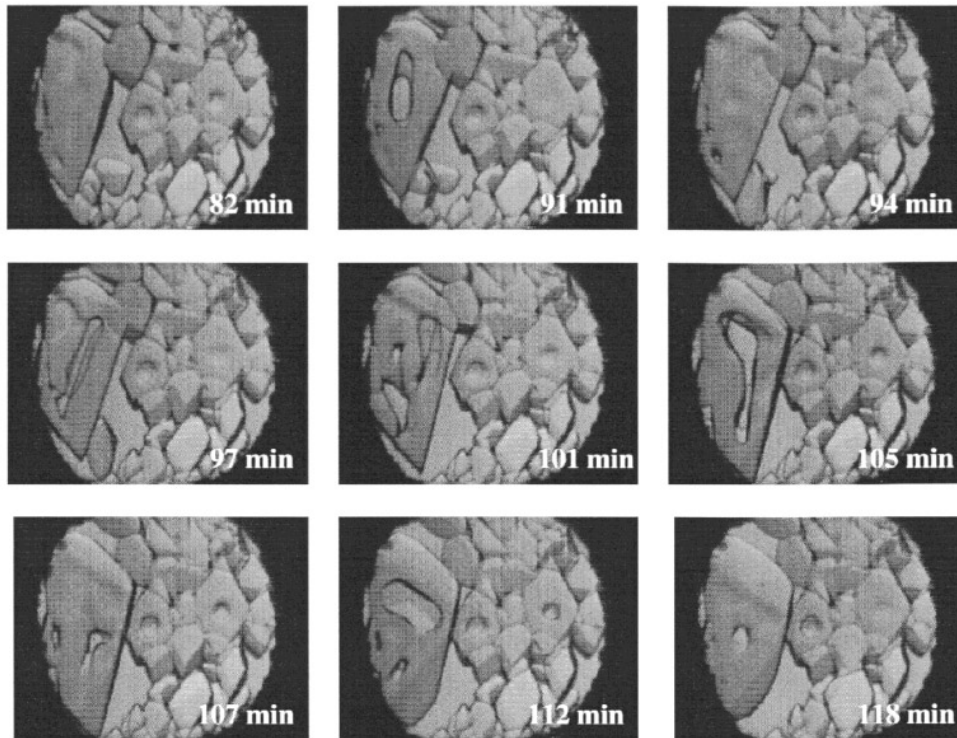


Figure 2. As in figure 1 but at times of 82, 91, 94, 97, 101, 105, 107, 112 and 118 min. The point to note is the melting and recrystallization of portions of the large crystal on the left as described in the text.

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 equilibrium with liquid. The case of a single (spherical) crystallite can however be solved and shows no possibility of melting within a crystallite [9]. This finding is consistent with the experimental fact that, after evolving to a 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.

In summary, we have observed dramatic temporal fluctuations involving melting and resolidification of liquids in equilibrium with their crystals at constant volume. The temporal nature of the fluctuations goes beyond the scope of previous theoretical treatments and require further theoretical work for their explanation. Our observations also provide supporting evidence for the existence of the recently predicted interparticle interaction during Ostwald ripening.

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