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## Kinetics of heterogeneous nucleation and the ‘memory effect’ in liquid gallium

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**Abstract.** A series of experiments on liquid gallium is briefly reviewed. A new approach to the behaviour of liquid gallium during the crystallization is explained and a model of kinetics of heterogeneous nucleation is presented. The experimental results obtained by use of the simple thermal analysis have fully confirmed this model.

### 1. Introduction

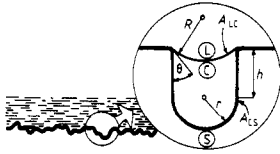
Liquid gallium exhibits several interesting properties and perhaps the most unusual of them is a high tendency to supercooling. The detailed investigations of this phenomenon have shown that the maximum temperature of supercooling (or the temperature at which freezing begins) is a function of the temperature at which the liquid is annealed above the melting point  $T_m = 303$  K [1, 2]. Moreover, if the liquid gallium is annealed at a temperature higher than  $T^* = 333$  K it prefers to freeze into the metastable  $\beta$ -phase. This kind of behaviour suggests that the liquid gallium just above  $T_m$ , cooled from the temperature  $T > T^*$ , is a different liquid from the liquid gallium just melted from the  $\alpha$ -phase.

We have investigated these phenomena by use of several techniques. The main aim of our earlier experiments was to find a physical quantity which could distinguish the liquid gallium melted from the  $\alpha$ -phase and the liquid gallium cooled down from a high temperature.

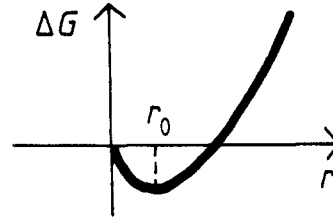
For samples obtained by various heat treatments, as described above, we have measured:

- (i) the static structure factor  $S(Q)$  by use of neutron diffraction [3];
- (ii) the heat capacity by use of accurate, adiabatic calorimetry [4];
- (iii) the inelastic neutron scattering spectra [5].

The result of all these experiments is that there are no differences between samples obtained by various heat treatments. This suggests that there are not two kinds of gallium liquid, but that the observed phenomena result from the complex nucleation process.



**Figure 1.** The cylindrical cavity as a model of substrate roughnesses.



**Figure 2.** Free energy of a crystal cluster as a function of the radius of the cavity.

This conclusion has turned our attention toward the kinetics of heterogeneous nucleation.

## 2. Theoretical model

The kinetics of heterogeneous nucleation has been thoroughly investigated by Turnbull [6, 7]. We can adopt his ideas to construct our model of the kinetics of heterogeneous nucleation on a non-flat surface.

In all our experiments the liquid gallium sample was placed in the teflon or vitreous silica (Pyrex) container. One can prove very easily that the liquid gallium wets both kinds of surfaces (as well as any other surfaces) very well. It allows us to assume that the liquid gallium fills up all the cavities existing on the surface of the substrate (it is evident that none of the real surfaces is perfectly flat). Let us consider a cylindrical cavity having the shape shown in figure 1.

When we try to obtain the change of free energy for the crystal cluster in such a cavity we get:

$$\Delta G = \Delta G_v + \Delta G_i$$

$$\Delta G_v = \Delta g V$$

$$\Delta G_i = A_{LC}\sigma_{LC} + A_{CS}\sigma_{CS} - A_{CS}\sigma_{LS}$$

where  $\Delta G_v$  and  $\Delta G_i$  are the volume and interface terms respectively,  $\sigma$  is the appropriate interface energy per unit area,  $\Delta g$  is the free energy difference between the liquid and solid phases per unit volume and  $V$  is the volume of the cluster.

Using the obvious relation between the interface energies:

$$\sigma_{LS} = \sigma_{CS} + \sigma_{LC} \cos \theta$$

where  $\theta$  is the wetting angle, and putting the geometrical formulae for volume and area, it is easy to show that:

$$\Delta G = \pi(\Delta g f_1 r^3 / 3 + (\Delta g h + 2\sigma f_2)r^2 - 2\sigma h f_3 r) \quad (1)$$

where:

$$f_1 = 2 - (2 - 3 \sin \theta + \sin^3 \theta) / \cos^3 \theta$$

$$f_2 = (1 - \sin \theta) / \cos^2 \theta - \cos \theta$$

$$f_3 = \cos \theta.$$

One can show that the relation for the free energy of a cluster obtained may have the

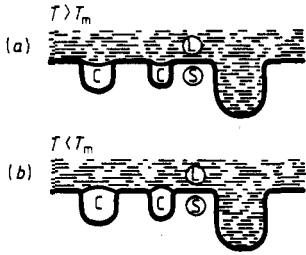


Figure 3. Behaviour of the solid phase remainders in the cavities with various diameters.

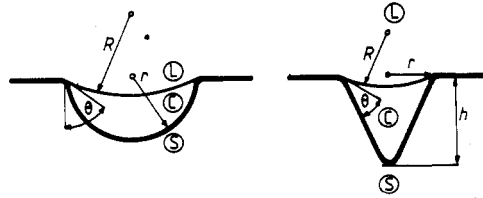


Figure 4. Model substrate roughnesses: (a) hemispherical cavity, (b) conical cavity.

form presented in figure 2, even for  $\Delta g > 0$  (for the temperature  $T$  higher than the melting point  $T_m$ ). This implies that the crystal clusters in such a way that the cavities can survive the melting point, only if the radius of the cavity is smaller than  $r_0$  (see figure 2). Considering the condition for the minimum of the function  $\Delta G$  versus  $r$ :

$$d(\Delta G)/dr = 0$$

which gives the following formula for  $r_0$ :

$$r_0 = [-(\Delta gh + 2\sigma f_2) + \sqrt{\Delta g^2 h^2 + 4\sigma^2 f_2^2 + 4\Delta gh\sigma f_2 + 2\Delta g f_1 \sigma h f_3}]/\Delta g f_1. \quad (2)$$

Using some approximations, this formula yields:

$$r_0 = \sigma \cos \theta / \Delta g. \quad (3)$$

If one takes into account that

$$\Delta g = s_f \Delta T^+$$

where  $\Delta T^+ = T - T_m$  and  $s_f$  is the entropy of fusion, it is easy to show that for a certain temperature of annealing  $\Delta T^+$ , the crystal clusters can survive the melting point  $T_m$  in the cavities with radius  $r$  fulfilling the condition: (see figure 3(a)):

$$r < \sigma \cos \theta / s_f \Delta T^+. \quad (4)$$

After cooling the liquid to the temperature  $T$  lower than the melting temperature  $T_m$ , the remainder of the solid phase in the cavities creates the clusters with maximum radius which is defined by: (see figure 3(b))

$$R < r / \sin \theta.$$

So, radii of the clusters fulfil the condition:

$$R < \sigma / s_f \operatorname{tg} \theta \Delta T^+.$$

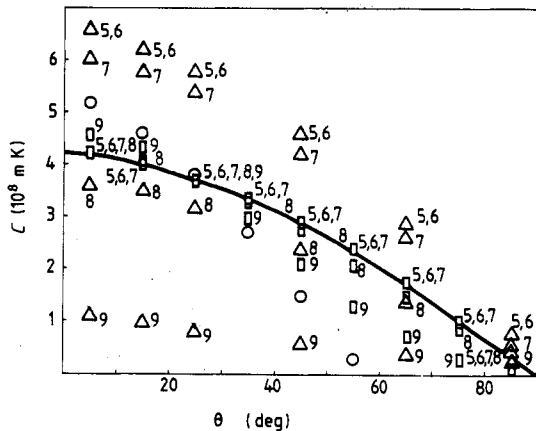
These clusters exceed the critical radius which is given by:

$$R^* = 2\sigma / s_f \Delta T^-$$

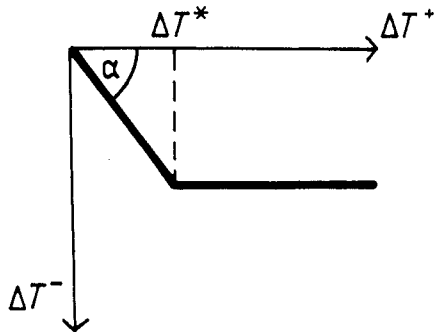
where  $\Delta T^- = T_m - T$  and become the nucleus for the temperature of supercooling  $\Delta T^-$  given by the simple equation:

$$\Delta T^- = 2 \operatorname{tg} \theta \Delta T^+. \quad (5)$$

It turns out that the temperature of maximum supercooling  $\Delta T^-$  is a linear function



**Figure 5.** Dependence of the parameter  $C$  (equation (6)) on wetting angle for various geometries of cavities. Numbers ( $n$ ) placed near the points mark the exponents characterizing the depth  $h$  of the cylindrical or conical cavity:  $h = 10^{-n}$  m. The full line is determined by the equation:  $C = \sigma \cos \theta / s_f$ ;  $\square$ : cylinder;  $\circ$ : hemisphere;  $\triangle$ : cone.



**Figure 6.** The model dependence of the temperature of supercooling  $\Delta T^-$  on the temperature of annealing  $\Delta T^+$ .

of the temperature of annealing in the liquid state  $\Delta T^+$ . The only variable parameter in this relation is the wetting angle  $\theta$ .

The analogous calculations have been done for two other geometries: the hemispherical cavity (figure 4(a)) and the conical cavity (figure 4(b)). For all considered geometries, the simple relation between the annealing temperature  $\Delta T^+$  and the radius of the cavity below which the remainder of the solid phase can survive the melting point, is obtained. This relation has the form:

$$r_0 = C / \Delta T^+ \quad (6)$$

where the parameter  $C$  is mainly a function of the wetting angle  $\theta$ . The dependence of the parameter  $C$  on the wetting angle  $\theta$  for various geometries of the cavities, using the values of  $s_f = 1.62 \times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$  [2] and  $\sigma = 6.77 \times 10^{-2} \text{ J m}^{-2}$  [8] for gallium is shown in figure 5.

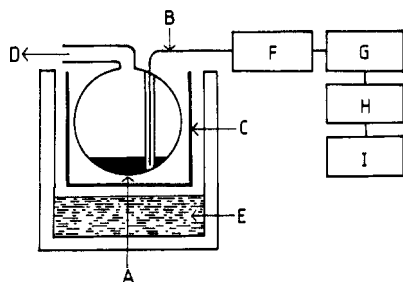
One can see that if the temperature of annealing  $\Delta T^+$  exceeds several dozen of kelvins, the radius  $r_0$  is smaller than 1 nm. This implies that the cavities, in which the solid phase could survive, are of the atomic dimensions; the existence of clusters or nuclei in such a cavity is out of the question. Thus, there is a maximum temperature of annealing  $\Delta T^*$ , above which the relation between  $\Delta T^-$  and  $\Delta T^+$  disappears.

So, the described model leads to the conclusion that the dependence of the temperature of supercooling  $\Delta T^-$  on the temperature of annealing  $\Delta T^+$  should have the form shown in figure 6.

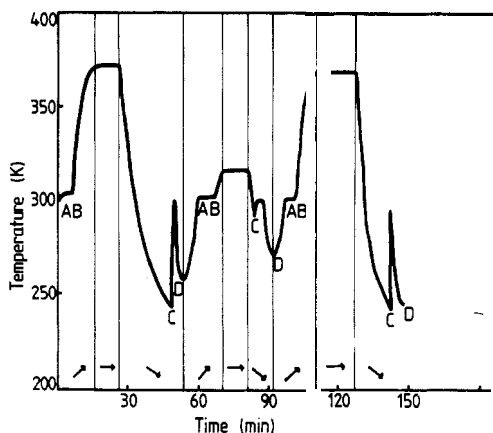
It is worth adding, that the conclusions from the proposed model are consistent with the well known relation between the interphase surface curvature  $K$  and the shift of the equilibrium temperature  $\Delta T$  [9]:

$$\Delta T = K \sigma / s_f.$$

Positive  $K$  leads to lowering of the equilibrium temperature—it is the case of spherical



**Figure 7.** Scheme of the apparatus for measurements by use of the simple thermal analysis. A: the sample; B: the thermocouple; C: the heater; D: vacuum; E: liquid nitrogen; F: the digital voltmeter; G: the interface; H: the computer; I: the printer.



**Figure 8.** The example variation of the temperature as a function of time. The gallium sample is placed on the Pyrex glass. Arrows in the bottom of the diagram mean: ↗: constant heating rate; →: constant temperature; ↘: constant cooling rate.

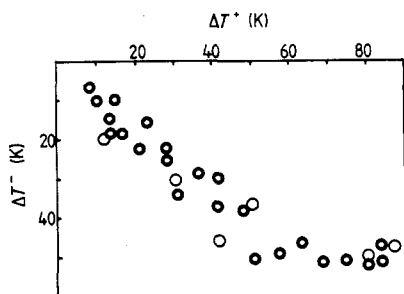
nucleus, which melts and freezes below the normal melting point. In the described model we have a negative interface curvature and this gives an increase of the melting temperature.

### 3. Experimental verification of the model

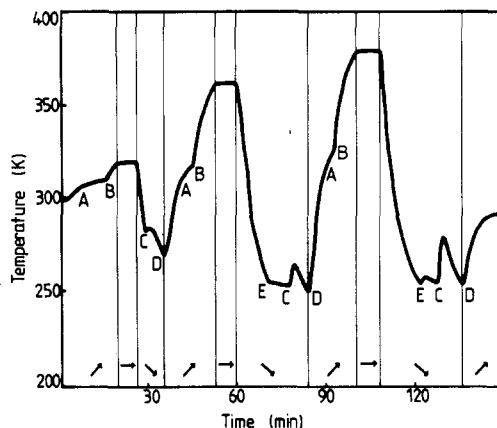
In order to verify the proposed model, the method of simple thermal analysis has been used; the apparatus is schematically shown in figure 7. The main feature of such measurements is that the sample is in contact with one kind of the substrate only, so that heterogeneous nucleation can occur with one characteristic wetting angle  $\theta$ . Besides, the atmosphere is well controlled and the influence of surface oxidation of the sample should be prevented. One can assume that the significance of uncontrolled external factors, which could initiate crystallization processes has been reduced considerably.

The measurements are made as follows: the sample was melted, then it was annealed at the chosen temperature and then it was cooled down with constant cooling rate. The example dependence of the temperature on the time is shown in figure 8. One can see that all first order phase transitions are evidently visible: melting (segment A–B) and freezing of the supercooled liquid with high heat emission (segment C–D). The dependence of the maximum temperature of supercooling on the temperature of annealing for gallium placed in a pyrex glass container, obtained by use of the described method, is shown in figure 9.

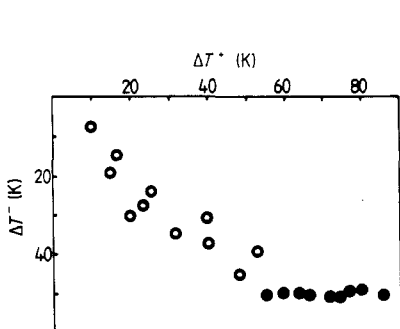
One could notice however, that the vacuum used here is too poor and gradual oxidation of the sample surface has occurred. In order to eliminate this effect, the new sample has been covered by a silicone oil layer. It should be mentioned, that the wetting angle of gallium on the Pyrex glass was not changed after this operation. The example of the temperature variation obtained with such conditions is shown in figure 10. The



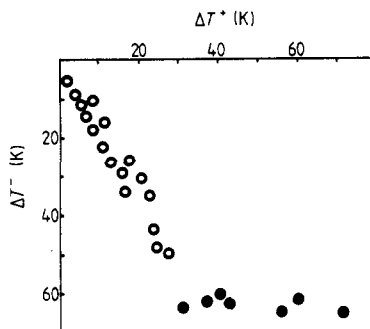
**Figure 9.** Experimental dependence of the temperature of freezing on the temperature of annealing for the gallium sample placed on Pyrex glass; ●: in air; ○: in vacuum.



**Figure 10.** The example variation of the temperature as function of time. The gallium sample is covered by a silicone oil layer.



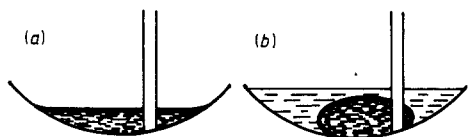
**Figure 11.** Experimental dependence of the temperature of freezing on the temperature of annealing for a gallium sample covered by a silicone oil layer; ○: freezing to the  $\alpha$ -phase; ●: freezing to the  $\beta$ -phase.



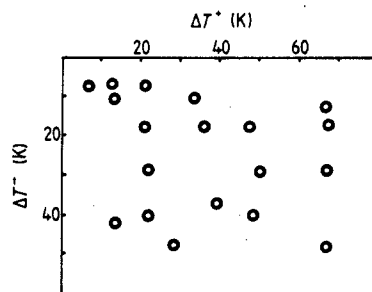
**Figure 12.** Experimental dependence of the temperature of freezing on the temperature of annealing for a gallium sample placed on a Teflon substrate; ○: freezing to the  $\alpha$ -phase; ●: freezing to the  $\beta$ -phase.

important difference is apparent during freezing: the temperature leap connected with crystallization to the  $\alpha$ -phase is preceded by a smaller heat emission (segment E-C in figure 9). Because this process occurs at a temperature 1–5 K below the  $\beta$ -phase melting point, it suggests the following explanation of the phenomena: the liquid gallium is supercooled below the melting point of the  $\beta$ -phase, it freezes (partly or completely) to this phase; because of its metastability, the further cooling provokes transition to the  $\alpha$ -phase (segment C-D in figure 10) again with high heat emission. This explanation is consistent with the fact that the heat of fusion for  $\alpha$ -Ga is more than twice as large as for  $\beta$ -Ga [10].

The results obtained in the way described are completed in figure 11. One can see very easily that the slope of the linear part of the relation between  $\Delta T^+$  and  $\Delta T^-$  is the same as in figure 9.



**Figure 13.** The shape of a gallium sample in the glass container; (a) in air, vacuum or in silicone oil; (b) in hydrochloric acid.



**Figure 14.** Experimental dependence of the temperature of freezing on the temperature of annealing for a gallium sample covered by hydrochloric acid.

The analogous measurements have been done for the sample placed on the Teflon substrate. It has been checked that the wetting angle  $\theta$  was somewhat larger for gallium placed on a Teflon surface than for gallium placed on a Pyrex glass surface. The obtained results are shown in figure 12. In this case, the sample has crystallized to the  $\beta$ -phase, if it has been kept in a pure helium atmosphere.

In order to check the importance of substrate wetting on the memory effect, another series of measurements has been carried out, in which the sample was covered by hydrochloric acid (concentration 5%). This caused complete lack of wetting of the glass by the liquid gallium, which can be confirmed by comparing the shape of the sample placed on pure glass (figure 13(a)) and for the sample placed in hydrochloric acid (figure 13(b)). The results obtained under these conditions are shown in figure 14: the complete lack of the memory effect is evident.

The wetting angles in all systems studied have been observed by taking photographs of the liquid gallium droplets laid on the flat surface. However, the accuracy of this method has been very poor. The estimated values of the wetting angles obtained have been completed below:

Liquid gallium on a Pyrex glass in vacuum	$30^\circ \pm 5^\circ$
Liquid gallium on a Pyrex glass in silicone oil	$30^\circ \pm 10^\circ$
Liquid gallium on Teflon in vacuum or helium	$40^\circ \pm 5^\circ$
Liquid gallium on Pyrex glass in HCl(aq)	$0^\circ$ to $5^\circ$ .

#### 4. Discussion of experimental results

One can conclude from the experimental results that the proposed model of the influence of wetting and heterogeneous nucleation on the memory effect is quite well confirmed. The agreement between experimental relations shown in figures 9, 11, 12 and the one obtained from the model (figure 6) is satisfactory. It seems that the existence of the oxide layer on the sample surface is responsible for the lack of possibility of crystallization to metastable  $\beta$ -phase. Comparing the slope of the linear part of the diagrams in figures 9 and 12, and the values of the temperature  $\Delta T^*$  for both cases, shows that the wetting



angle for Teflon substrate is bigger than for the Pyrex one, which is in agreement with the wetting angle observations. The correlation between lack of wetting and lack of memory effect is evident in figure 14. Besides, there is no memory effect if only homogeneous nucleation is permitted—this is the case of the liquid gallium droplets in dispersive media [11, 12].

It should be underlined, that only the high purity of our samples allows us to obtain such results; in our measurements gallium with purity of 99.9999% has been used.

The influence of the annealing time and the cooling rate on the freezing temperature has also been investigated. It turned out that an annealing time longer than five minutes and a cooling rate varying in the very wide range:  $20 \text{ K min}^{-1}$ – $1 \text{ K h}^{-1}$  are not able to change the temperature of maximum supercooling. It is unexpected perhaps, but this point has been checked very carefully: the temperature of freezing is really independent of the cooling rate. It depends only on the temperature of annealing.

In the end of the discussion one important question should be answered: why should just gallium show the memory effect? This effect is the result of coexistence of two factors, which are generally in contradiction: the substrate must be very well wetted by the liquid (this is necessary for filling all the substrate cavities by liquid) and the liquid must show high ability for supercooling. For pure gallium both conditions are fulfilled, because it well wets almost all clean surfaces and the nucleation of crystals is hindered because of quite different atomic arrangements in the liquid and solid phases. Indeed, the short range order in liquid and solid gallium is completely different, which has been confirmed by many diffraction [13, 14] and EXAFS [15, 16] experiments.

## 5. Conclusions

The proposed model of correlation between wetting the substrate by the liquid and the memory effect has been tested experimentally and is in good agreement with the obtained results. It seems that processes accompanying the crystallization of gallium are well understood; all experimental results are coherent and agree with the described model of kinetics of heterogeneous nucleation.

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