

# Experimental and numerical study of anomalous thermocapillary convection in liquid gallium

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Thermocapillary Marangoni convection of liquid gallium was studied experimentally and numerically. A specially designed experimental setup ensured an oxide-free surface of the liquid gallium for a very long time. The convective flow at the free surface was found to be directed opposite to both buoyancy-driven and ordinary thermocapillary convection. The anomalous direction of the thermocapillary flow was explained by the presence of a small amount of a surface-active contaminant—lead adsorbed at the free surface. Two different approaches were used to describe the observed phenomenon. First, the flow was treated as a pure thermocapillary convection with a modified dependence of the surface tension on temperature so that to reproduce the measured velocity distribution. Second, a novel physical model was devised for the flow driven by the gradient of the surface tension induced by the temperature dependence of the concentration of the adsorbed layer of contaminant. In contrast to the ordinary thermocapillary convection in low-Prandtl-number liquids, there is a strong coupling between the flow and the driving force in the proposed model resulting in velocity profiles very similar to those observed in the experiment.

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## I. INTRODUCTION

Thermocapillary convective flows are encountered in many technological processes involving free surfaces of a liquid with a nonuniform temperature distribution. Widespread interest in these flows is related with manufacturing of semiconductor monocrystals in a microgravity environment.<sup>1,2</sup> Up to now most experimental studies of thermocapillary flows were carried out on transparent liquids (e.g., silicon oils, acetone, decane, etc.—see Refs. 3–11 and references therein) having Prandtl numbers usually larger than 10. However, semiconductor melts have small values of the Prandtl number, of the order of  $10^{-2}$ . In experiments on fluids with low Prandtl number<sup>12–15</sup> no data on flow patterns (even steady state convection) have been reported yet. The main difficulty in conducting experiments with thermocapillary convection in liquid metals and semiconductors is the oxidation rapidly covering the free surface with a rigid oxide film that renders it stagnant. Another experimental difficulty is related with the opaqueness of such liquids. In the present work we deal with liquid gallium which is considered as a

model fluid to study Marangoni convection, as well as it is technologically significant for manufacturing compound gallium-based semiconductors.

A specially designed experimental setup ensuring an oxide-free free surface of liquid gallium for a very long time (up to six months) was used in the present study (see Sec. II). This enabled us to monitor the motion of tracer particles along the free surface and to measure the corresponding velocity profiles. It turned out that the movement along the free surface is directed from the cold toward the hot area for some temperature range just above the melting temperature. This finding was quite unexpected, since it means that surface tension increases with temperature. In the most investigations, however, the surface tension of gallium is found to decrease with increasing temperature.<sup>16–21</sup> An exception is a weak increase of the surface tension with increasing temperature in the 400–500 °K interval reported in Ref. 17, where it was attributed to the effect of impurities. However, it is necessary to note that even in the most accurate experimental studies<sup>16</sup> there are only few measurements of the surface tension of gallium in the range of 100 °C above the melting point, where the variation of the measured surface

tion does not exceed the experimental accuracy. Although the linear decrease of surface tension at higher temperatures is an experimentally well established fact, there seem to be no definite experimental data about the variation of the surface tension close to the melting point.

The unusual course of the thermocapillary flow was initially attributed to an anomalous temperature dependence of surface tension. Most of the measurements of the surface tension coefficient of gallium have been done for temperatures far above its melting point of 29.8 °C. In the experiments described the gallium was about 10 °C overcooled. Experimental data on the surface tension of the overcooled gallium<sup>16</sup> shows a nonmonotonous behavior. Another possible reason for the anomalous temperature dependence of surface tension might be presence of a surface-active contaminant. A possible source of contamination in the present experiment is a short contact of gallium with lead. This could lead to a very low impurity concentration, which, however, is able to affect strongly the surface tension. Strong effect of contamination on the temperature dependence of surface tension was reported for gallium with solid carbon islands in Ref. 20 and with lead in Ref. 32, and for other liquid metals and semiconductors in Refs. 22–26. In particular, in Ref. 23 growth of the surface tension with temperature was reported for cadmium, in Ref. 24—for Ag–Pb systems, in Refs. 25 and 26—for steel with sulfur and oxygen impurities (the latter two works are relevant for welding processes). For welding processes it was established that about 100 ppm of sulfur in steel lead to reversed direction of the thermocapillary flow. Note also that practically all measurements of the surface tension of gallium were done using a sessile or pendent-drop method under steady-state conditions at a fixed temperature. In such situations a steady equilibrium concentration of impurity at the surface is reached. In the present work the conditions are different. The impurity is advected by the flow and the equilibrium can never be reached. Therefore, in the case of a slightly contaminated surface the temperature dependence of surface tension should be different from that measured in static experiments, and is unknown. Since the surface concentration of the contaminant depends on the surface temperature (see Sec. III B) one can try to replace the dependence of the surface tension on both concentration and temperature by a temperature dependence only. The corresponding effective temperature dependence of surface tension is considered in Sec. III A. A more consistent model involving surface tension dependence on both concentration of an adsorbed contaminant and temperature is presented in Sec. III B. With an appropriate choice of two phenomenological parameters this model reproduces the experimentally measured profile of the surface velocity. Concluding remarks are summarized in Sec. IV.

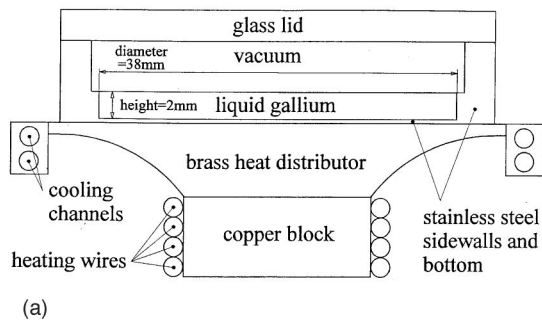
## II. DESCRIPTION OF THE EXPERIMENT

### A. Experimental setup

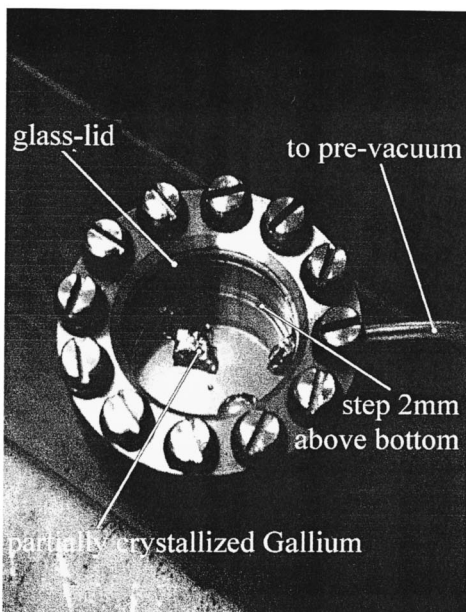
A sketch and a photograph of the special experimental container are shown in Fig. 1. Using a sophisticated high-vacuum technique,<sup>27</sup> liquid gallium was filled into the container with an optical window shown in Fig 1. The main idea

was to obtain an oxide-free surface. For this purpose the working container was made as small as possible, so as to minimize the total amount of residual gas molecules. The filling facility comprised a pool of molten gallium (99.99% purity) and a pipeline connecting it with the working container through a U-shaped tube. The container, (outer diameter of about 80 mm and a height of 20 mm) was made of stainless steel and closed with an optical polished glass lid. The thickness of the container bottom was 0.5 mm. The system was sealed by a lead gasket between the upper surface of the container and the lid. The filling facility was placed inside a standard vacuum chamber with minimal residual pressure less than  $10^{-6}$  Torr. The gallium in the pool was degassed at 300 °C for 48 h, with the pressure down to  $5 \times 10^{-7}$  Torr at the end of this procedure. The pool temperature was then lowered to 100 °C, and at a residual pressure of  $10^{-6}$  Torr the liquid gallium was drawn through the pipeline into the working container which had previously undergone a similar degassing procedure at 200 °C. The amount of gallium introduced into the container was such as to form a layer of 2 mm thickness. To keep the oxide film out of the pipeline, extreme precautions were taken to keep its inlet completely immersed. Prior to opening the vacuum chamber, the gallium in the U-shaped tube was solidified by cooling with liquid nitrogen. After that, vacuum in the working container was ensured by connecting the outlet of the pipeline to a pre-vacuum reservoir ( $10^{-3}$  Torr) with the solidified gallium in the U-shaped tube serving as a safe seal. Note that even when the residual pressure in the container is as high as  $10^{-6}$  Torr, the ratio of the total number of residual gas atoms to that of gallium atoms on the surface is less than  $10^{-3}$ , and no continuous oxide film can form, while the discrete oxide particles which do form on the surface are used as tracers in the experiment. This finite-volume technique is the principal advantage and innovation versus all other methods used before. Sealing of the container by the pre-vacuum reservoir was further improved by filling the copper cylinder up with activated charcoal, so that it serves as an adsorption getter pump. Attached to the outlet of the pipeline, it worked so well that no deterioration of the surface quality was noticeable over 6 months after preparation of the facility.

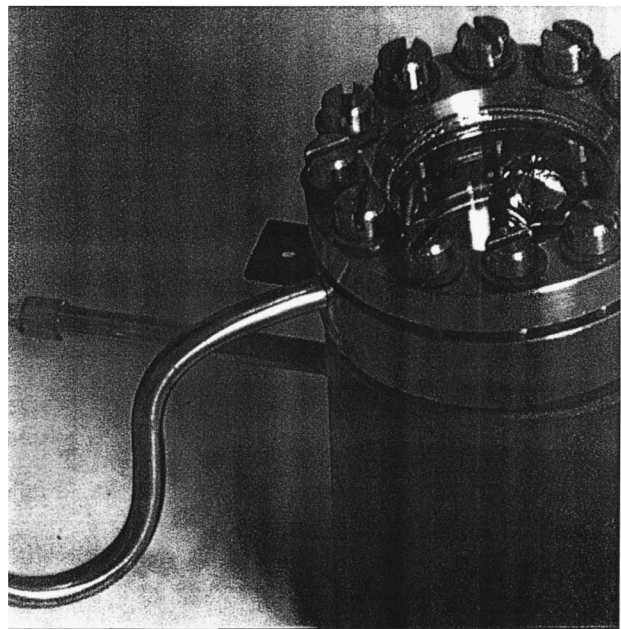
To achieve the driving temperature difference needed for the thermocapillary experiments, the container was placed on a specially designed brass heat distributor, creating an axisymmetric linear temperature gradient along the container bottom. Such a temperature distribution was obtained by using a conical heat distributor with height varying as  $z \sim r^{-2}$ . The apex was cut off, and the remaining frustum was installed in an upside-down position with the gallium container on its flat base as shown in Fig. 1(a). Filling the gap between them with In–Ga–Sn eutectic melt which is liquid at room temperature ensured good thermal contact between the heater and the container bottom. At the outside radius of the container the frustum was cut off along a vertical line. This outer cylindrical surface together with the sidewall of the container was surrounded by a circular channel to which cooling water was supplied at high flow rates. The bottom of the heater (the surface where the apex was cut off) was fixed onto a filament heater and the jacket of the cone was ther-



(a)



(b)



(c)

FIG. 1. Sketch (a) and photographs (b) and (c) of the experimental setup.

mally insulated. The heat flux through the cone from the heater to the cooler remaining nearly constant while the vertical cross section of the cone decreases as  $\sim 1/r$  implies a radial temperature gradient  $\sim r$ . Up to the experimental accuracy, such a gradient was confirmed by temperature measurements in the gap between the surface of the heat distributor and the bottom of the container, as well as inside an open container filled with gallium. The temperature in the gap was measured by Ni–NiCr wires with the In–Ga–Sn providing the electrical contact between the electrodes, and inside the container with a copper–constantan thermocouple with 0.2 mm diam bonded to the container bottom.

## B. Experimental results

After heating was switched on, motion of solid particles (with characteristic size about 0.1 mm) was observed along the free surface of the gallium. These particles probably consisted of gallium oxide or some intermetallic gallium compound (such as Ga–Pb, see below). The particles moved from the side wall towards the maximum of the temperature

in the center of the container, where they eventually converged creating an island. The observed direction of fluid flow was opposite to buoyancy convection as well as to ordinary Marangoni convection. To continue the experiment, it was necessary to redistribute the particles. One way of redistribution was to switch the heater off and wait until the tracers spread over the surface. Some of the particles adhered to the wall, and migrated one by one towards the center when the temperature gradient was restored. Another way of redistribution was to stir the melt by using the interaction of externally applied magnet with thermoelectric currents circulating through the melt and container. The particle motion was recorded on videotape. An example of streakline picture is shown in Fig. 2. The radial velocity of the flow was determined from the length of the streaks on the photographs and the known exposure time. The measured velocity profile is shown in Fig. 3. The measurements were carried out for temperatures 20 °C at the rim and 50 °C at the center of the container bottom.

When the temperature at the bottom center increased up

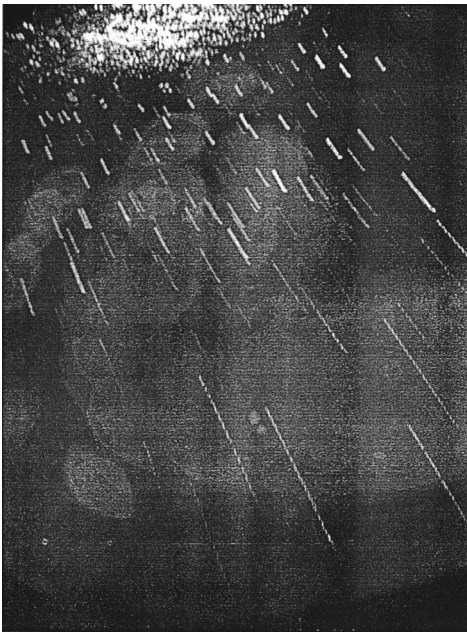


FIG. 2. Streaklines at the free surface of liquid gallium at characteristic temperature difference between the center and rim 30 °C. The container wall is seen as a semicircle at the bottom of the photograph. The particles tend to collect at the center of the container (top left part of the photograph).

to 200 °C, transition from axisymmetric to asymmetric three-dimensional flow was observed. The corresponding photo of the streaklines is shown in Fig. 4. The observed surface flow consists of four quadruple-like oscillating vortices.

### III. THEORETICAL MODELS AND NUMERICAL RESULTS

The main goal of the theoretical and numerical analysis was to explain the anomalous pattern of the surface velocity (Fig. 3) with the tracer particles moving from cold to hot regions. First, we tried to find a simplest possible temperature dependence of the surface tension reproducing the measured velocity profile. Such a construction is based on the assumption that the observed flow is a pure thermocapillary convection that however cannot be taken for granted in the case under consideration. So we also developed a novel physical model which is able to explain consistently the experimental observations by the presence of an adsorbed layer of contaminant on the surface of the gallium. In this model,

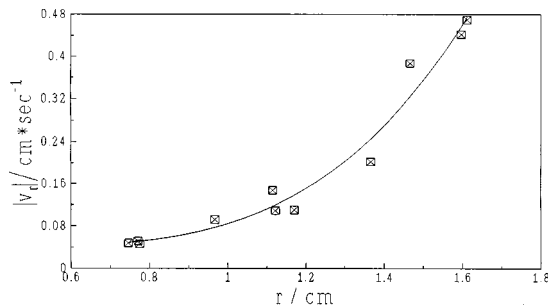


FIG. 3. Results of the measurement of the radial velocity magnitude at the free surface of liquid gallium for the characteristic temperature difference 30 °C.

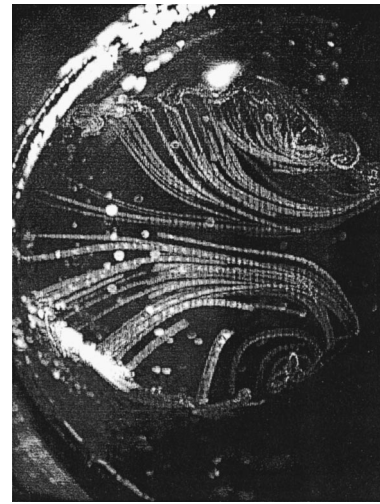


FIG. 4. Streaklines at the free surface of liquid gallium. The container wall is seen as a semicircle on the left. The particles move from the wall to the center. The characteristic temperature difference is 180 °C.

the gradient of the surface tension is induced by the variation of the surface concentration of adsorbed contaminant, which in turn depends on the temperature.

#### A. Formulation of the problem for Marangoni-buoyancy convection and results of numerical simulation

The steady axisymmetric convective flow is described by a set of dimensionless Boussinesq equations in the cylinder  $0 \leq r \leq A$ ,  $0 \leq z \leq 1$

$$(\mathbf{v} \cdot \nabla) \mathbf{v} = -\nabla p + \Delta \mathbf{v} + Gr \theta \mathbf{e}_z, \quad (1)$$

$$(\mathbf{v} \cdot \nabla) \theta = \frac{1}{Pr} \Delta \theta, \quad (2)$$

$$\nabla \cdot \mathbf{v} = 0, \quad (3)$$

which is considered together with the equation for steady temperature distribution

$$\Delta \theta = 0, \quad (4)$$

inside the bottom ( $0 \leq r \leq A + \bar{d}$ ,  $-\bar{h} \leq z \leq 0$ ) and the side wall ( $1 \leq r \leq \bar{d}$ ,  $0 \leq z \leq 1$ ) of the container. Here  $\mathbf{v} = (u, w)$ ,  $\theta$  and  $p$  are dimensionless velocity, temperature and pressure, respectively;  $Gr = g\beta(T_1 - T_2)H^3/\nu^2$  and  $Pr = \nu/\kappa$  are Grashof and Prandtl numbers;  $A = R/H$  is the aspect ratio,  $g$  gravity acceleration,  $\beta$  the thermal expansion coefficient,  $(T_1 - T_2)$  the temperature difference between the center and rim of the container bottom,  $\nu$  kinematic viscosity,  $\kappa$  thermal diffusivity,  $H$  the depth of the gallium layer,  $R$  the inner radius of the container,  $\bar{h} = h/H$ ,  $h$  the thickness of the bottom and  $\bar{d} = d/H$ ,  $d$  the thickness of the side wall. The velocity is scaled by  $\nu/H$ , whereas the dimensionless temperature is defined as  $\theta = (T - T_2)/(T_1 - T_2)$ .

A quadratic radial temperature distribution is prescribed at the outer surface of the container bottom

TABLE I. Physical properties of liquid gallium at 30 °C.

Property	Source	Value
Dynamic viscosity, $\eta$	Ref. 30	$2.13 \times 10^{-3} \text{ N s m}^{-2}$
Density, $\rho$	Ref. 30	$6.11 \times 10^3 \text{ kg m}^{-3}$
Heat capacity, $c_p$	Ref. 30	$0.36 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1}$
Thermal conductivity, $\lambda$	Ref. 30	$28.33 \text{ W m}^{-1} \text{ K}^{-1}$
Thermal expansion coefficient, $\beta$	Ref. 30	$1.17 \times 10^{-4} \text{ K}^{-1}$
Kinematic viscosity, $\nu$	$= \eta/\rho$	$3.5 \times 10^{-7} \text{ m}^2/\text{s}$
Thermal diffusivity, $\kappa$	$= \lambda/c_p\rho$	$1.29 \times 10^{-5} \text{ m}^2/\text{s}$
Prandtl number, $Pr$	$= \nu/\kappa$	0.027
Temperature coefficient of surface tension $\gamma = \partial\sigma/\partial T$	Ref. 16 (4 ÷ 40 °C)	$0.0068 \text{ N m}^{-1} \text{ K}^{-1}$
	Ref. 17 (200 ÷ 600 °C)	$0.00606 \text{ N m}^{-1} \text{ K}^{-1}$
Aspect ratio, $A$	$= R/H$	10
Relative thickness of the bottom, $\bar{h}$	$= h/H$	0.25
Relative thickness of the wall, $\bar{d}$	$= d/H$	0.25

$$\theta = 1 - \left(\frac{r}{A}\right)^2 \quad \text{at} \quad z = -\bar{h}. \quad (5)$$

$$u = \frac{\partial w}{\partial r} = \frac{\partial \theta}{\partial r} = 0 \quad \text{at} \quad r = 0. \quad (11)$$

The outer surface of the side wall, as well as the free surface of the gallium are assumed to be perfectly thermally insulated

$$\frac{\partial \theta}{\partial z} = 0 \quad \text{at} \quad z = 1, \quad (6)$$

$$\frac{\partial \theta}{\partial r} = 0 \quad \text{at} \quad r = A + \bar{d}, \quad (7)$$

and continuous heat flux is prescribed at the inner surfaces of the bottom and side wall

$$\left. \frac{\partial \theta}{\partial z} \right|_{z=0+} = \bar{\lambda} \left. \frac{\partial \theta}{\partial z} \right|_{z=0-} \quad \text{and} \quad \left. \frac{\partial \theta}{\partial r} \right|_{r=A-} = \bar{\lambda} \left. \frac{\partial \theta}{\partial r} \right|_{r=A+}, \quad (8)$$

where  $\bar{\lambda} = \lambda_{\text{steel}}/\lambda_{\text{gallium}}$  is the heat conductivity ratio of the wall and liquid, respectively. No-slip boundary conditions for the velocity are assumed at the bottom and side wall

$$\mathbf{v} = 0 \quad \text{at} \quad z = 0 \quad \text{and} \quad r = A. \quad (9)$$

Since there were no noticeable deformations of the free surface in the experiment, we consider the free surface as flat. For arbitrary temperature dependence of the surface tension, the Marangoni boundary condition at the free surface of the gallium may be written in the dimensionless form as

$$\frac{\partial u}{\partial z} = Ma \frac{\partial \bar{\sigma}}{\partial \theta} \frac{\partial \theta}{\partial r}, \quad (10)$$

where  $Ma = \gamma(T_1 - T_2)H/(\rho\nu^2)$  is the Marangoni number based on the characteristic temperature coefficient of the surface tension  $\gamma = -(\partial\sigma/\partial T)_{T=T_0}$  taken at some reference temperature  $T_0$ ;  $\bar{\sigma}$  is the dimensionless surface tension scaled by  $|\gamma(T_1 - T_2)|$ . In the classical case of the surface tension decreasing linearly with the temperature, we have  $(\partial\bar{\sigma})/(\partial\theta) = -1$ .

To complete the formulation of the problem, symmetry boundary conditions are prescribed at the container axis:

Problems (1)–(11) was solved by the finite volume method, which is of the second order in space and time, and had been validated and successfully used in Refs. 28 and 29.

Physical properties of liquid gallium are listed in Table I. For the characteristic temperature difference of 30 °C, the Grashof number can be estimated as  $Gr \approx 2250$ , which was the value used in further calculations.

For the Marangoni number calculated on the basis of the literature data,<sup>16,17</sup>  $Ma \approx 1.5 \times 10^4$ , the thermocapillary flow moves against the direction observed in the experiment with the characteristic surface velocity higher than the observed one (shown in Fig. 3). This implies that the temperature dependence of the surface tension for gallium is anomalous because of either overcooling like for cadmium<sup>23</sup> or contamination by some surfactant as reported in Refs. 24–26,31.

First, we assumed the flow to be a pure thermocapillary convection driven by the following nonlinear surface tension dependence on the temperature:

$$\sigma(T) = \sigma_0 - \gamma(T - T_0) - \gamma_1(T - T_0)^2 - \gamma_2(T - T_0)^3, \quad (12)$$

which is a straightforward generalization of the classical linear dependence. Then boundary condition (10) takes the form

$$\frac{\partial u}{\partial z} = -Ma(1 + \bar{\gamma}_1(\theta - \theta_0) + \bar{\gamma}_2(\theta - \theta_0)^2) \frac{\partial \theta}{\partial r}, \quad (13)$$

where the dimensionless coefficients are defined as  $\bar{\gamma}_1 = 2(T_1 - T_2)\gamma_1/\gamma$  and  $\bar{\gamma}_2 = 3(T_1 - T_2)^2\gamma_2/\gamma$ . It was found that the observed velocity distribution can be reproduced well using Eq. (12) with  $T_0 = 25$  °C,  $Ma = -300$ ,  $\bar{\gamma}_1 = 0$  and  $\bar{\gamma}_2 = 8.33$ . The corresponding values of the dimensional parameters are  $\gamma \approx -2.9 \times 10^{-6} \text{ N m}^{-1} \text{ K}^{-1}$ ,  $\gamma_1 = 0$ ,  $\gamma_2 \approx -9 \times 10^{-8} \text{ N m}^{-1} \text{ K}^{-3}$ . This means that the surface tension increases with temperature. The numerical results are shown in Fig. 5 in comparison with the experimental data. The corresponding flow pattern is shown in Fig. 6. Note that there is a

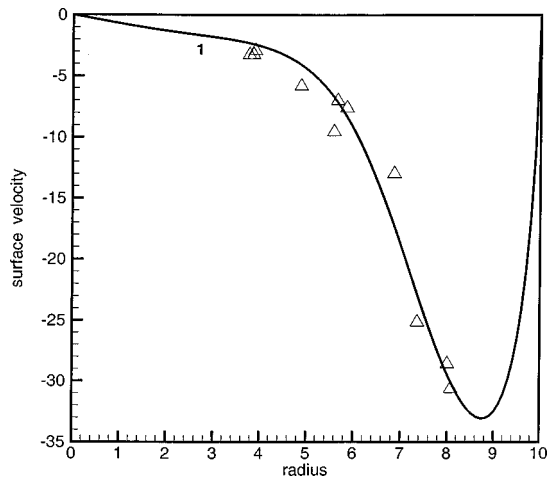


FIG. 5. Calculated profiles of the surface velocity compared with the experimental data. Computation on  $100 \times 20$  uniform grid.  $\Delta$ -experimental data taken from Fig. 3; 1-cubic dependence  $\sigma(T)$ ,  $Gr=2250$ ,  $Ma = -300$ ,  $\bar{y}_1=0$ ,  $\bar{y}_2=8.33$ ,  $T_0=25^\circ\text{C}$ .

secondary vortex close to the center and driven by the buoyancy which is suppressed by the thermocapillary flow at the free surface.

The described numerical results indicate that for a complete explanation of the experimental observations even such a generalized temperature dependence of the surface tension, which in addition was never observed in any steady-state equilibrium experiments with pure gallium, is not sufficient. A more consistent description of the experimental results is provided in the following subsection by a model taking into account a contaminant adsorbed at the free surface.

### B. Capillary convection due to thermally induced nonuniformity of an adsorbed layer

Despite the high purity of the gallium, laser-ablation analysis of the solidified sample of gallium done after opening of the container revealed 0.5% of lead in the layer of 50 microns depth at the free surface, but no lead in the bulk of the sample was found. This contamination might be due to accidental contact of the gallium with the lead seal during filling of the container. Even a brief contact would be enough for the detected concentration. No copper, iron or nickel were found in the surface layer. The only detected element besides lead was cadmium, but its concentration was three orders of magnitude smaller than that of the lead.

It has to be emphasized that the analysis of the solidified gallium revealed neither lead nor any other elements in the bulk of the material down to the resolution limit of 1 ppm. It means that any element analysis of the bulk material would lead to the conclusion that we were dealing with gallium of very high purity. The laser ablation analysis is particularly well suited to detect surface contamination.



FIG. 6. Streamlines of the calculated convective flows for,  $Gr=2250$ ,  $Ma = -300$ ,  $\bar{y}_1=0$ ,  $\bar{y}_2=8.33$ ,  $T_0=25^\circ\text{C}$ .

Lead is known to be strongly surface active with respect to gallium, and even a very small admixture can significantly change the surface tension of the latter. Our goal for this subsection is to work out the simplest possible theory of thermocapillary flow in the presence of a soluble adsorbed layer of a substance on the surface. The surface concentration of the adsorbed layer depends on both the temperature and bulk concentration:  $C_s = C_s(C, T)$ . In the presence of a dissolved contaminant the surface tension is no longer a function of temperature alone, but also of the concentration of the impurity in the bulk:  $\sigma = \sigma(T, C)$ . Taking into account the previous relation, we can express the surface tension as  $\sigma = \sigma(T, C_s)$ . Since surface-active substances are known to affect surface tension much more intensively than temperature, we can assume that the surface tension is affected exclusively by the surface concentration:  $\sigma = \sigma(C_s) = \sigma(C_s(T, C))$ . Thus, some temperature dependence is retained, but in contrast to the usual case, the considered dependence of the surface tension consistently leads to increase of the latter with temperature, whereas in the previous subsection this was simulated in a semi-empirical manner only. Indeed, the thermodynamic stability of such an adsorbed layer requires  $(d\sigma)/(dC_s) < 0$ , i.e., the surface tension must decrease with concentration of the adsorbed layer. Otherwise, a small surface concentration increment will increase the surface tension, which in turn will cause the adsorbed layer to converge and increase the surface concentration further. As a result, a small initial perturbation would cause collapse of the adsorbed layer. The stability of thermodynamic equilibrium also implies  $(\partial C_s)/(\partial T) < 0$ . In the opposite case, a perturbation in the form of a partial dissolution of the adsorbed layer causing a temperature decrease (because of increase of the entropy at a fixed internal energy) will escalate and lead to complete dissolution of the layer. Hence,  $(\partial\sigma/\partial T) = (d\sigma/dC_s)(\partial C_s/\partial T) > 0$ . The above considerations are in agreement with the recent experimental findings for Ga–Pb system.<sup>32</sup> This explains the observed anomalous direction of the flow: In the center of the container, where the temperature is higher, the adsorbed layer partly dissolves and its concentration decreases, so that the surface tension increases, driving the surface towards the center of the container. This centripetal flow advects the adsorbed layer and restores its concentration, and at the same time reduces gradient of the surface tension. When the surface concentration exceeds its equilibrium level, the surfactant on the surface begins to dissolve, increasing the bulk concentration. The resulting nonuniformity of the latter is smoothed out by diffusion and advection of the impurity in the liquid bulk. Thus there is a balance between contraction and stretching of the adsorbed layer, as well as between adsorption and desorption of the impurity—which is controlled by its diffusion from and to the surface. Since the diffusion of the impurity is much slower than the thermal or even the viscous one, the flow has a very strong feedback on the driving force. This is different from pure thermocapillary convection in low-Prandtl-number fluids where the coupling between the velocity and the driving temperature field is weak. The strong coupling in the present case could account for the heavily concave surface velocity profile observed in the experiment.

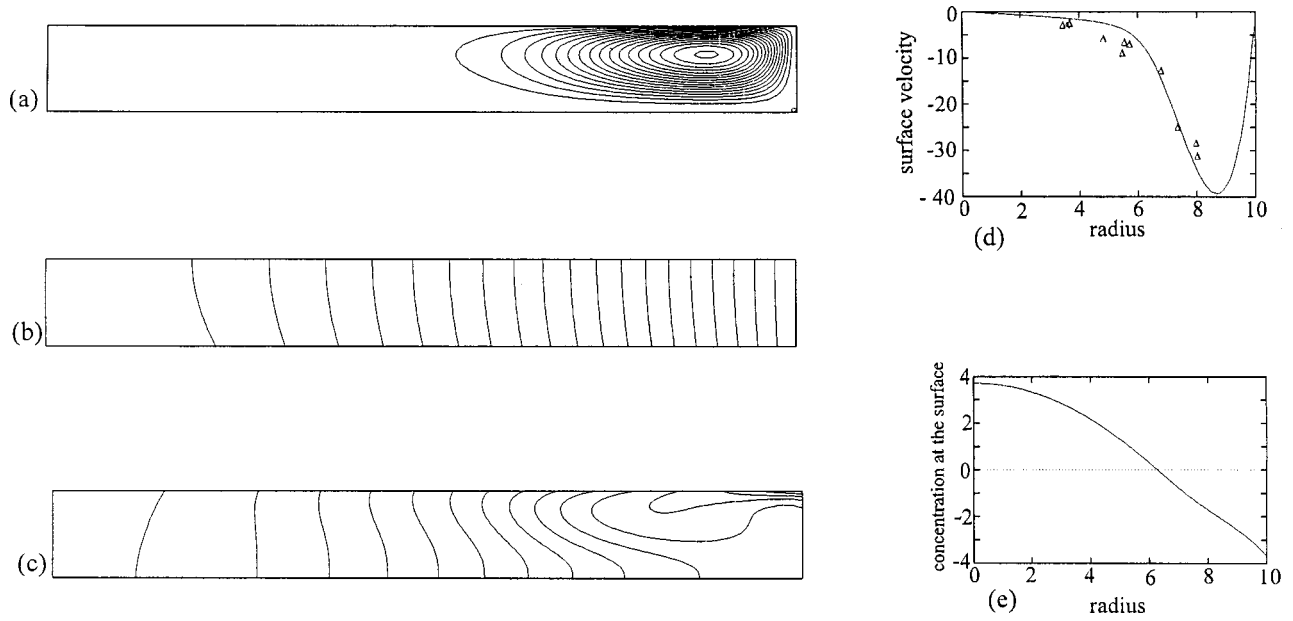


FIG. 7. Results of the calculation based on the model incorporating a surfactant layer.  $Mq=100$ ,  $Sc=100$ ,  $\chi=1$ . (a)—streamlines, (b)—isotherms; (c)—isolines of the bulk concentration; (d)—profile of the surface velocity, shown by the curve as conjugated to the experimental data from Fig. 3 (symbols); (e)—bulk concentration at the surface.

To put the above considerations in quantitative form, we introduce an additional couple of rather common assumptions. First, the temperature and concentration deviations from the thermodynamic equilibrium are assumed to be small, so that linear approximation is applicable

$$C_s(C, T) = \frac{\partial C_s}{\partial T}(T - T_0) + \frac{\partial C_s}{\partial C}(C - C_0), \quad (14)$$

where  $T_0$  and  $C_0$  are the reference values for the temperature and bulk concentration, respectively. Then the radial gradient of the surface tension may be written as

$$\frac{\partial \sigma}{\partial r} = \beta_T \frac{\partial T}{\partial r} - \beta_C \frac{\partial C}{\partial r}, \quad (15)$$

where  $\beta_T = (d\sigma/dC_s)(\partial C_s/\partial T) > 0$  and  $\beta_C = -(d\sigma/dC_s) \times (\partial C_s/\partial C) > 0$ . For  $\beta_C \neq 0$ , the surface tension depends also on the bulk concentration in addition to the temperature. To find the concentration, we must solve the diffusion-convection equation for the dissolved substance under the conservation condition for the adsorbed layer. Further we assume the variation of the surface concentration to be small compared to its characteristic value:  $C_s(C, T) \approx C_s(C_0, T) = C_{s,0}$ , which yields

$$\frac{1}{r} \frac{\partial(ruC_s)}{\partial r} \approx \frac{C_{s,0}}{r} \frac{\partial(ru)}{\partial r} = D \frac{\partial C}{\partial z}, \quad (16)$$

where  $D$  is the diffusion coefficient for the impurity. The above expression states that there is an impurity flux from the free surface into the bulk, where the material surface is being compressed ( $\partial(ru)/\partial r < 0$ ), and a reverse flux where it is being stretched ( $\partial(ru)/\partial r > 0$ ). Since the total area of the free surface remains constant, the opposite fluxes are balanced and the total flux from the free surface is zero. At all the other boundaries zero impurity flux is assumed corre-

sponding to  $\partial C/(\partial n) = 0$ . This completes the formulation of the problem for the bulk concentration. Note that the concentration is determined by Eq. (16) up to an additive constant (depending on the initial conditions), but this constant has no effect on the fluid flow in the model under consideration.

To complete the mathematical formulation for dimensionless variables, we have to add the equation of transport for the concentration in the bulk

$$(\mathbf{v} \cdot \nabla)C = \frac{1}{Sc} \Delta C \quad (17)$$

(where  $Sc = D/\nu$  is the Schmidt number) to the Boussinesq set [Eqs. (1)–(3)] with the boundary conditions for the concentration [including Eq. (16)]

$$\begin{aligned} \frac{\partial C}{\partial z} = 0 \quad \text{at } z=0, \quad \frac{\partial C}{\partial r} = 0 \quad \text{at } r=0, A, \\ \frac{\partial C}{\partial z} = \frac{1}{r} \frac{\partial(ru)}{\partial r} \quad \text{at } z=1, \end{aligned} \quad (18)$$

where the bulk concentration is scaled by  $\Delta C = Sc^{-1}C_{s,0}/H$ . The boundary condition (10) should be replaced by

$$w=0, \quad \frac{\partial u}{\partial z} = Mq \left( \frac{\partial \theta}{\partial r} - \chi \frac{\partial C}{\partial r} \right) \quad \text{at } z=1, \quad (19)$$

where  $Mq = (\beta_T(T_1 - T_2)H)/\rho\nu^2$  is analogous to the usual Marangoni number;  $\chi = (\beta_C \Delta C)/(\beta_T(T_1 - T_2))$  is referred to as the coupling parameter between the temperature and concentration effects. The case  $\chi=0$  corresponds to the ordinary thermocapillary convection with a negative sign of the Marangoni number. Besides the Schmidt number, this formulation comprises two phenomenological parameters:  $Mq$  and  $\chi$ . Further we choose the Schmidt number  $Sc=100$

as a characteristic value for the Ga–Pb system. The other two parameters,  $Mq$  and  $\chi$ , which to the best of our knowledge have not been measured for the lead-gallium system, are varied to adjust the computations to the experimental data. In the present computations the parameter  $Mq$  was chosen to match the magnitude of the observed velocity, while the coupling parameter  $\chi$  was adjusted to reproduce the observed shape of the velocity distribution at the free surface. The results of the calculation based on the described model are shown in Fig. 7. It can be seen that the proposed model not only gives the right direction of the flow, but is also able to reproduce the characteristic shape of the velocity distribution with a stagnant zone at the center of the container, where the flow converges [cf. Fig. 7(a) with Fig. 6].

#### IV. CONCLUDING REMARKS

The conducted experimental study of thermocapillary convection of liquid gallium showed an anomalous flow direction at the free surface. This can be explained by increase of the surface tension with temperature that is unusual for liquid semiconductors and is in contradiction to most of the reported temperature dependencies of surface tension for liquid gallium.<sup>18–21</sup> Only the data of Ref. 16 for the temperature range corresponding to the overcooled gallium, and the data of Ref. 17 in a higher temperature range show an increase of the surface tension of liquid gallium with temperature. Therefore, the overcooling of the gallium can be a possible reason for the anomalous temperature dependence of the surface tension. An appropriate temperature dependence may be found to fit the experimental data. Another possible reason for the abnormal flow could be contamination of the free surface of gallium by a very small amount of lead as shown in Ref. 32. It was already conjectured in Ref. 17 that the anomalous temperature dependence of surface tension, experimentally obtained for a certain temperature interval, might be due to an impurity in the gallium. Such anomalous dependencies for molten steel due to contamination by sulfur and oxygen were observed in welding processes.<sup>25,26</sup> It is difficult to figure out whether the surface contamination of gallium by lead is similar to the effect of sulfur on the surface tension of steel,<sup>25</sup> since in the case of the present work lead is mostly adsorbed on the free surface. To address the effect of contamination we developed a novel physical model for the flow driven by the surface tension gradient induced by the temperature variation of the adsorbed layer of a surface active substance. The proposed model consistently reproduces both the right direction of the flow and also the characteristic shape of the surface velocity profile having a stagnant zone in the center of the container where the flow converges.

Although the surface-active contaminant (lead) was accidental, the described experimental and numerical results permit an important conclusion about thermocapillary convection in liquid semiconductors. As a rule, manufactured semiconductors contain a very small amount of dopant. The results of the present work show that the surface tension itself, as well as its temperature dependence, can be strongly affected by the dopant (lead) and differ significantly from

those for the pure material (gallium). In the case of the gallium-lead system this can even lead to change of sign of the temperature coefficient of the surface tension and to the appearance of thermo-concentration-capillary flows directed from cold to hot areas, as was found and explained in the present work. Similar effects were recorded before for steels with a sulfur content of about 100 ppm,<sup>25</sup> lead-silver systems,<sup>24</sup> and 99.9999% cadmium.<sup>23</sup> To the best of our knowledge, similar effects were never reported for liquid semiconductors. A phenomenological model describing such effects is proposed here for the first time.

Transition from axisymmetric to three-dimensional flow (as illustrated in Fig. 4) can be studied as it was done in Refs. 33 and 34. However, before such an analysis is undertaken, the surface tension of the overcooled gallium should be carefully measured, and the proposed model for the phenomenon should be verified as rigorously as possible.

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