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THE POSSIBILITY OF CREATING CONDITIONS OF PERMANENT SENSITIVITY OF SUPERCOOLED LIQUIDS TO CHARGED PARTICLES

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The possibility of creating conditions of permanent sensitivity of supercooled liquids to charged particles by setting up a certain temperature gradient in the liquid is analyzed theoretically. Some theoretical demands on the geometric characteristics of the system, and the choice of working liquid and material of the walls and top are established. Formulas are given for calculation of the upper and lower temperatures of the sensitivity zone. The width of the latter is determined.

INTRODUCTION

PISAREV[1] has shown the possibility of the appearance of ions in supercooled liquids. This phenomenon was proposed for use for the creation of a tracking apparatus, capable of detecting moving charged particles. Just as in [2] there were revealed physical conditions for the permanent sensitivity of binary liquid solutions to ions, it is possible to analyze the possibility of obtaining constant sensitivity of supercooled liquids to charged particles. One can obtain a zone of permanent sensitivity by creating a definite temperature gradient in appropriate liquids. In the present paper, the possibility of obtaining such conditions is analyzed theoretically.

THE TEMPERATURE GRADIENT AND CONVECTIVE STABILITY

We consider a vertical cylindrical column of liquid, along which a constant temperature gradient is maintained. At the lower end of this column, we maintain some temperature T_l which should be greater than T_0—the fusion temperature, and at the upper end, the temperature T_2, which is the lower boundary of the temperature sensitivity zone of a supercooled liquid to charged particles. T_2 is the minimal temperature of supercooling, beyond which the formation of a solid phase occurs effectively even without any isolated centers; T_1 is the upper limit of the temperature sensitivity zone, beginning with which the effective formation of a solid phase takes place on the charged centers. The liquid in the zone between T_0 and T_2 is in a metastable supercooled state. The temperature distribution is shown schematically in the drawing. If such conditions can exist, then the charged particle passing through the sensitivity zone between T_1 and T_2 and producing ionization, leaves behind it a chain of growing crystallites.[1] The produced crystals will grow so long as they are in the zone of the metastable state. Under the action of the force of gravity, they will fall downward and enter a zone with temperature above the melting temperature, where they will melt. Most materials expand on heating and therefore their density decreases here. Therefore, it is important to make clear the problem of the convective stability of a similar system. The problem of the conditions for the appearance of stationary convection in a motionless liquid in a vertical cylindrical tube, along which a constant temperature gradient is maintained, was investigated by Ostroumov.[3,4] It has been shown that, to avoid convective flow of the liquid, it is necessary that the temperature gradient be parallel to the gravitational force. The instant of appearance of convection corresponds to the smallest value of the quantity

$$\gamma = PG = AR^4 g\alpha / \chi\nu. \tag{1}$$

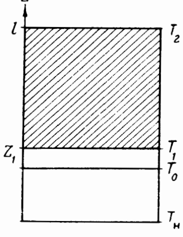
Here P is the Prandtl number, G the Grasshof number, $\partial T/\partial Z = -A < 0$ is the temperature gradient, R the radius of the cylinder, g the acceleration due to gravity, α the coefficient of thermal expansion of the liquid, χ the coefficient of thermal conductivity, and ν the kinematic viscosity.

In the limiting case of thermally insulated walls, $\gamma = 67.4$. In the other limiting case (infinite thermal conductivity of the walls) $\gamma = 215.8$. Thus, if the difference $(T_l - T_2)$ is not too large, the cylinder is sufficiently high, and its radius is sufficiently small, then the liquid remains motionless, and a purely thermally conducting regime develops. The temperature and the density of the liquid in this case are functions of the coordinate Z, while the density of the liquid above is higher than below.

We find the temperature distribution along the column of liquid. In the absence of convection and of heat sources inside the liquid, the equation of thermal conductivity is

$$\Pi = -\varkappa \operatorname{grad} T, \tag{2}$$

where Π is the heat flux, κ the coefficient of thermal



Vertical temperature distribution. The sensitive zone is shaded.

conductivity of the liquid. We then have

$$\operatorname{div} \Pi = 0, \quad \partial^2 T / \partial Z^2 = 0. \tag{3}$$

Integration of the second of Eqs. (3) for our boundary conditions gives

$$T(Z) = T_l - \frac{T_l - T_2}{l} Z, \tag{4}$$

l is the length of the liquid column.

Thus, to each value of Z from Eq. (4), one can set a definite temperature T, and conversely, for T one can find the corresponding Z, i.e., the height at which the given temperature is achieved.

LIMITING TEMPERATURES OF THE SENSITIVITY ZONE

As the upper temperature boundary of sensitivity of a supercooled liquid to charged particles, we take such a temperature T_1 for which the crystallites, which are formed on ions, would be visible, independent of their dimensions. The upper temperature boundary is determined from thermodynamic considerations in [1]:

$$T = T_0 \left[1 - \frac{3}{2} \frac{M}{\rho Q} \left(\frac{4\pi\sigma^4}{(ze)^2} \frac{\varepsilon_1 \varepsilon_2}{(\varepsilon_2 - \varepsilon_1)} \right)^{1/3} \right] . \tag{5}$$

Here M is the molecular weight of the crystallizing material, ρ its density, Q the molar heat of fusion, σ the surface tension on the "crystal-liquid" boundary, ze the charge of the particle on which crystallization occurs, ϵ_1 and ϵ_2 the dielectric constants of the liquid and the crystal. Substituting T_1 from (5) in (4), we get an expression for finding the location of the lower boundary of the sensitivity zone, corresponding to the upper temperature boundary,

$$Z_1 = \left\{ T_l - T_0 \left[1 - \frac{3}{2} \frac{M}{\rho Q} \left(\frac{4\pi\sigma^4}{(ze)^2} \frac{\varepsilon_1 \varepsilon_2}{(\varepsilon_2 - \varepsilon_1)} \right)^{1/3} \right] \right\} (T_l - T_2)^{-1} l. \tag{6}$$

We further determine the lower temperature boundary corresponding to the spontaneous production of crystals. We make use of the results of the theory of heterophase fluctuations[5] in the case of phase inversion of "liquid-crystal" from the melt. According to this theory, even up to the beginning of the usual phase transition, the system keeps the new nucleation phase in the metastable state, i.e., strictly speaking, it is inhomogeneous. The presence of the new nucleation phase and its distribution are considered not as fluctuations, but as the appearance of statistical equilibrium of the system.

Just as in [2], we make use of the Becker–Döring solution of the fundamental kinetic equation for the rate of formation of critical nuclei and apply it to the phase inversion "liquid-crystal:"

$$I = \frac{S^* \beta}{(2\pi kT)^{1/2}} \sqrt{\frac{\Delta\Phi^*}{3n^*}} N \exp\left(-\frac{\Delta\Phi^*}{kT}\right). \tag{7}$$

Here I is the number of critical viable nuclei of crystals forming per cm^3 per second, S^* is the surface area of the critical nucleus (in the case of a spherical nucleus, $S^* = 4\pi r^2$), β the number of collisions of the molecules of the liquid with unit surface of the nucleus per second, $\Delta\Phi^*$ the maximum change in the thermodynamic potential of the system in the formation of a critical nucleus in the supercooled liquid (the height of the potential barrier which must be surmounted by the system in order that a nucleus of critical size be formed), n^* the number of molecules in the critical nucleus, N the number of molecules in 1 cm^3 of the liquid, k Boltzmann's constant.

Let us determine $\Delta\Phi^*$. The change in the thermodynamic potential of the system in the formation of a critical nucleus of radius r in the supercooled liquid is

$$\Delta\Phi = -(\mu_1 - \mu_2) N_M + S\sigma, \tag{8}$$

where μ_1 is the molar chemical potential of the liquid phase, μ_2 the molar chemical potential of the crystalline phase, N_M the number of moles in the nucleus, S the surface of the nucleus. $N_M = \frac{4}{3}\pi r^3 (M/\rho)^{-1}$, where M/ρ is the volume of a single mole of the crystal, $(\mu_1 - \mu_2) = Q\Delta T / T_0$, ΔT the supercooling of the liquid. Taking it into account that at the maximum $\partial(\Delta\varphi)/\partial r = 0$, we find the critical radius of the crystalline nucleus and the maximum change in the thermodynamic potential:

$$r^* = \frac{2\sigma M/\rho}{Q\Delta T/T_0}, \tag{9}$$

$$\Delta\Phi^* = \frac{16}{3} \pi\sigma^3 \left(\frac{M/\rho}{Q\Delta T/T_0} \right)^2. \tag{10}$$

The number of molecules in the critical nucleus is

$$n^* = \frac{4}{3}\pi r^{*3} (M / \rho N_0)^{-1}. \tag{11}$$

Here N_0 is Avogadro's number, $M/\rho N_0$ the volume occupied by one molecule of the material in the crystal.

The number of molecules in the supercooled liquid in 1 cm^3 is

$$N = N_0 \rho_{\mathrm{liq}} / M, \tag{12}$$

where ρ_{liq} is the density of the liquid.

We now determine the mean number of collisions of molecules of the supercooled liquid with a unit surface per second. The growth of the crystal nucleus presupposes the preliminary separation of the molecules growing on the crystal from those of the surrounding liquid. The "activation energy" necessary for this separation, is identical with the energy which is the prerequisite of self-diffusion of molecules of the liquid. The fraction of molecules found in a similar "activated" condition is determined by the expression $\exp(-\Delta U/\kappa T)$, where ΔU is the "activation energy." Taking this into account, we can assume[5]

$$\beta = \beta_0 \exp(-\Delta U / kT), \tag{13}$$

where $\beta_0 = N\sqrt{kT/2\pi m}$, m is the mass of a single molecule From the viewpoint of the theory of heterophase fluctuations, the value $\Delta U \approx \lambda$ where $\lambda = Q/N_0$ is the heat of fusion referred to a single molecule.

Substituting (9)–(13) in (7), we get an expression for the rate of formation of viable critical nuclei in 1 cm^3:

$$I = \frac{8}{\sqrt{6m}} \left(\sigma \frac{\rho_l}{\rho} \right)^2 \left(\frac{N_0}{Q\Delta T/T_0} \right)^{3/2} \exp - \left[\frac{\Delta U}{kT} + \frac{16\pi\sigma^3}{3kT} \left(\frac{M/\rho}{Q\Delta T/T_0} \right)^2 \right]. \tag{14}$$

We now define the lower temperature boundary as the temperature at which a number of critical nuclei of order of unity are formed in the supercooled liquid per cm^3 per second. Then, we can determine from (14) the corresponding supercooling $\Delta T^* = T_0 - T_2$ and consequently, the temperature T_2. In view of the transcendental character of (14), the problem is solved either graphically or numerically. We note that the rate of formation of critical nuclei is very much dependent on the supercooling of the liquid. As the factor in front of the exponential is not large, it would still be compensated by a rather small supercooling ΔT.

Application of Eq. (14) to the case of supercooled liquid argon, for which the upper temperature boundary was calculated in [1], shows the practical suitability of this liquid for the purpose of detecting moving charged particles if the calculated data used were sufficiently accurate. For argon, the temperature T_2 is found to be higher than T_1 for the charges of the nucleus of the crystallization centers 1e, 2e, 3e, 4e. The physical meaning of this result can be interpreted in the following fashion. The formation of the viable nuclei of the argon crystals on charged centers is somewhat more probable than spontaneous crystallization, but these probabilities are comparable. For this reason, for practical detection of moving charged particles, liquids should be used for which $T_1 > T_2$.

The rate of formation of viable nuclei I depends rather strongly on the value of the surface tension on the "crystal–liquid" interface. Therefore, by using reference data, we can take into account the dependence of the surface tension on the temperature. We note that in the theory developed above, we did not take into consideration the dependence of the surface tension on the dimensions of the nucleus. In calculations of the upper temperature boundary T_1 from (5), it should be taken into account that for small critical nuclei, the values of the dielectric constants ϵ_1 and ϵ_2 can differ appreciably from their macroscopic values.

EFFECT OF WALLS AND IMPURITIES

It is known that the appearance of a new phase in phase transitions, including crystallization from the melt, proceeds more easily on the walls and on various mechanical impurities. This is due to the fact that the work of formation of a critical nucleus is somewhat less in this case. The work involved in the formation of a critical nucleus is especially greatly reduced if the material of the walls or impurity particles has a suitable structure on some faces with the crystallizing material. All this must be taken into account in the choice of materials of the walls and covers, so as to obtain significant supercooling. The liquid used should be carefully cleansed of impurities. The materials of the walls and cover should be such that the liquid employed wets these substances but little. The temperature of the upper cover should be somewhat lighter than that calculated from Eq. (14).

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