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ON ION DETECTION IN SUPERCOOLED LIQUIDS

by

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In 1909 Frischauer(1) noticed that radium beta-rays help to accelerate the crystallisation of super-cooled sulphur. Later, in 1924, Bol'shanina and Kuznetsov at Tomsk State University continued Frischauer's investigations in pure piperine, which under normal conditions is easily super-cooled and does not crystallise for a long time. They showed(2) that exposing the super-cooled piperine to radium beta-rays also brought about a sharp increase in the number of crystallisation nuclei. The authors of paper(2) gave a qualitative explanation of the effect observed. In their opinion, centres of crystallisation due to density fluctuations in the super-cooled liquid become more stable if they acquire a charge. To the molecular cohesive forces in the crystal are added contracting electric forces induced by the charge.

The crystallisation effect in super-cooled liquid exposed to radiation has recently also been investigated experimentally by Varshneya(3). He carefully super-cooled pure water to -20°C and exposed it to C_o^{60} gamma-quanta. In the irradiated parts of the water crystalline needles appeared, which extended into the interior of the liquid along a collimated gamma-quanta beam.

In contrast to the ion mechanism initiating crystallisation, described in paper(2), the basis of the nucleation of needle crystals in the experiment performed by Varshneya is another well-known effect. The probability of fluctuation nucleation of centres of crystallisation with the lowering of the temperature of the liquid at first increases and then, after reaching a maximum, is reduced because of the increased viscosity of the medium.

If such a strongly super-cooled liquid is slightly heated, there is a strong probability that centres of crystallisation will again appear in it. In Varshneya's experiment gamma-rays served as heat sources, heating the super-cooled water locally in the places where the molecules were ionized and excited. Varshneya proposed to use this phenomenon for observing radiation fluxes. However, in spite of the originality of this proposition, it should all the same be mentioned that regular use of super-cooled liquid as a medium for detecting ionising radiation would be extremely difficult. In fact, owing to steady super-cooling the liquid will be liable to crystallise spontaneously and also in response to many random weak external influences, such as vibration, ultra-violet light, gamma-background etc. Furthermore, as is known, the speed of dissipation of heat energy in liquid is extremely high and the speed of growth of crystals low. Therefore, in order to create an appreciable probability of the formation of crystals in super-cooled liquid it is necessary to activate the diffusion of its molecules intensively. This is possible only with a large flux of strongly ionising radiation. Finally, the feasibility of artificially stopping the growth of crystals in the ionised parts of the liquid and of dissolving these crystals reversibly without heating the liquid appears problematic.

In this connection it seems interesting to return to the idea of Bol'shanina and Kuznetsov concerning the initiation of crystallisation nuclei by a charged electric field and to analyse this idea in the light of present-day phase transition theory. Such an analysis can substantially help to solve the problem of the search for a more complete and controllable method of observing radiation fluxes in liquids.

In fact, ions are produced in all liquids traversed by charged particles. A large part of the ions rapidly recombine after production, but 1-3% remain free for 10^{-4} - 10^{-3} sec or more(4 - 9). The long-lived ions create a conduction current in the liquids, and this effect is often used, for instance, in liquid dosimeters for measuring the charged particle flux(10,11). A certain part of the free ions accidentally combine in twos, threes or more. The number of such multiply charged complexes, as shown by investigations(9-12), represents a few percent of the total quantity of long-lived ions, and there are about 30-50 of these multiply charged formations in 1 cm. of the path of a relativistic particle. Thus, if the assumption concerning the initiation of crystallisation by charges is correct, one can expect the long-lived ions to be centres of crystal nucleation in rapidly super-cooled liquid.

2. Probability of the appearance of centres of crystallisation on the charges in di-electric liquid.

The probability that a stable crystallisation nucleus will appear in super-cooled liquid is(13):

$$W = n^{*} n \sqrt{\sigma k T} \sqrt{2v/9\pi} \; 1/h \exp\left(-\frac{U+A}{kT}\right) \qquad (1)$$

where n is the density of molecules in the liquid, n* the number of molecules in the surface layer of the nucleus, σ the surface tension on the crystal-liquid boundary, U the activation energy for characteristic diffusion of the molecules in the super-cooled liquid, A the variation of the thermodynamic potential of the liquid when crystal nuclei are produced in it, k the Boltzmann constant, h Planck's constant, T the temperature of the liquid and ν the volume of the atom of the initial phase. From(14) it follows that in expression (1) the values which depend on the electric field will be n and A, and to a lesser degree n* and U. Therefore in the subsequent analysis we shall restrict ourselves to examining the dependence of W on n and A only.

In accordance with papers(14 and 15)

$$A = N(\mu_2 - \mu_1) + \sigma S + \Delta U_{el} , \qquad (2)$$

where N is the number of gram-molecules of the liquid developing into crystalline nuclei, μ_1 and μ_2 the gram-molecule chemical potentials of the super-cooled liquid and the crystal respectively, S the surface of the nucleus and ΔU_{el} the variation of the free energy of the electric field of the charge present in the crystal nucleus. If the volume of the nucleus is v and the volume of one gram-molecule of the crystal is V, then N = V/v. Considering that V = M/ρ and S = $4\pi r^2$, where M is the gram-molecular weight of the nucleus, ρ is its density and r the radius of the nucleus (to simplify the problem under consideration let us assume that the crystal nuclei are of spherical shape), one will have:

$$A = 4\pi r^2 \sigma - \frac{4}{3}\pi r^3 \frac{\rho}{M} (\mu_1 - \mu_2) + \Delta U_{el} \qquad (3)$$

For single-component systems $\mu_1 - \mu_2 = q_n \Delta T / T_0$, where q_n is the melting point, $\Delta T = T_0 - T$ the degree of super-cooling of the liquid, and T_0 the normal crystallisation temperature. By substituting this expression in (3) we have:

$$A = 4\pi r^2 \sigma - \frac{4}{3}\pi r^3 \frac{\rho}{M} \frac{q_n \Delta T}{T_0} + \Delta U_{el} \qquad (4)$$

The density of the energy of the electric field with a strength E in a dielectric with a dielectric constant ε is $\varepsilon E^2/8\pi$. Therefore, the variation of the energy of the electric field when crystal nuclei are produced in the super-cooled liquid is:

$$\Delta U_{el} = \int_{v} \frac{\varepsilon_2 E_2^2}{8\pi} dv + \int_{V_0-v} \frac{\varepsilon_1 E_1^2}{8\pi} dv - \int_{V_0} \frac{\varepsilon_1 E_1^2}{8\pi} dv \qquad (5)$$

Here v, is again the volume of the nucleus, and V_0 is the total volume of the liquid before the formation of the nucleus, ε_1 is the dielectric constant of the liquid phase and ε_2 of the solid phase. It is evident that the field inside the crystalline particle bearing a charge ze will be $E_2 = ze/\varepsilon_2 r_x^2$, and the field in the medium $E_1 = ze/\varepsilon_1 r_x^2$.

By integrating equation (5) we obtain

$$\Delta U_{el} = -\frac{(ze)^2}{2}\left(\frac{\varepsilon_2-\varepsilon_1}{\varepsilon_1\varepsilon_2}\right)\left(\frac{1}{a}-\frac{1}{r}\right) \qquad (6)$$

where a is the ion radius, Since a is always smaller than r, it follows from (6) that when $\varepsilon_2 > \varepsilon_1$ crystallisation on the charge is accompanied by a gain of electric energy, and when $\varepsilon_2 < \varepsilon_1$ by a loss.

For the subsequent analysis it is convenient to introduce the following notation

$$A_1 = 4\pi r^2\sigma - \frac{4}{3}\pi r^3 \frac{\rho}{M} \frac{q_u \Delta T}{T_0} \qquad (7a)$$

$$A_2 = \frac{(ze)^2}{2}\left(\frac{\varepsilon_2-\varepsilon_1}{\varepsilon_1\varepsilon_2}\right)\left(\frac{1}{a}-\frac{1}{r}\right) \qquad (7b)$$

Let us now determine in formula (1) the value n when the liquid carries an electric charge. It is well known (see, for instance, (14)) that the charge once it has entered the liquid is solvated, and this leads to variation of the density of the medium in its vicinity. The approximate equation describing this effect has the form:

$$n(r) = n_0 \exp[-\psi(r, R)/kT], \qquad (8)$$

where n (r) is the density of the liquid in the solvated complex, n_0 the density at some distance from the charge, R the size of the solvated formation and ψ the potential energy of the solvation of the charge in the liquid. By substituting (7) and (8) in (1), we have:

$$W = n^{*} n_0 \sqrt{6kT} \sqrt[3]{2v/9\pi}\, 1/h \exp\left(-\frac{A_1 + U}{kT}\right) \exp\left(\frac{A_2 - \psi}{kT}\right) \qquad (9)$$

From this expression it follows that the ratio of the probability of the apparition of crystalline particles in supercooled liquid on ions W(ze) to the probability of the nucleation of centres of crystallisation upon density fluctuations W(0) is :

$$\frac{W(ze)}{W(0)} = \exp\left(\frac{A_2 - \psi}{kT}\right) \qquad (10)$$

For an overwhelming number of liquids $\psi < 0$ and A_2, as is seen from (7b), can be either positive or negative depending on the kind of liquid. The absolute value is

$$|A_2| \approx |\psi| \approx 0{,}3\ kT \quad [14, 18]$$

A. Dipolar liquids and liquids with anisotropic electric polarizability.

In the majority of liquids of the kind mentioned the statistical dielectric constant ϵ_1 is greater than the dielectric constant of its crystals ϵ_2 , which is due to the loss of the rotational degree of freedom in the molecule upon super-cooling. For this reason, in accordance with formula (7b), A_2 is less than zero. Therefore, in expression (10) $A_2 - \psi \cong 0$ and, consequently,

$$W(ze) / W(0) \cong 1.$$

This approximate equation indicates that the power of polar liquids and liquids with asymmetrical molecules to crystallize should not be markedly sensitive to the presence of charges in them.

B. Nondipolar or weakly polar liquids and liquids with isotropic electric polarizability.

For these liquids usually $\epsilon_2 > \epsilon_1$. since when they freeze the medium thickens, while the polarizability of the molecules is preserved. Therefore, in agreement with (7b), A_2 is greater than zero and $A_2 - \psi \approx 2\psi \approx 0.6$ kT. Calculation according to formula (10) gives: $W(ze)/W(0) > 1$. Hence it follows that there should be an appreciably greater probability of the formation of crystalline nuclei on electric charges in these liquids, than on fluctuations of the density.

3. Degree of super-cooling of the liquid necessary for the formation of crystals on ions.

Let us now find the equation for determining the super-cooling of the liquid ΔT necessary for crystallisation on ions and ion complexes such as nuclei to begin. For this purpose let us substitute relation (6) in formula (4), differentiate the expression obtained over r and equate to zero. The equation $\partial A / \partial r = 0$ will correspond to the fact that a crystal nucleus of the size $r = r_0$ is in equilibrium with the super-cooled liquid. Having carried out the above-mentioned operations and performed simple transforms, we obtain

$$\Delta T = \frac{T_0 M}{\rho q_n} \left[\frac{2\sigma}{r_0} - \frac{(ze)^2}{8\pi r_0^4} \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1 \varepsilon_2} \right] \qquad (11)$$

From this expression, using the standard method of determining the extreme function, we find

$$\Delta T_{max} = \frac{3}{2} \frac{T_0 M}{\rho q_n} \sqrt{\frac{4\pi\sigma^4}{(ze)^2} \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_2 - \varepsilon_1}} \qquad (12)$$

The sense of this equation from a physics angle is as follows: with super-cooling exceeding the value T_{max}, all nuclei, however small, formed on ions will grow indefinitely.

Let us now consider the method of super-cooling a liquid by rapid variation of the pressure on its surface.

4. Pulsed super-cooling of a liquid

The degree of super-cooling of a liquid necessary for the detection of ions can be achieved by rapidly applying to the liquid pressure which displaces its freezing point. Thus the connection between the value of the super-cooling of the liquid $\Delta T = T_0 - T$ and the value of the pressure drop $\Delta P = P - P_0$ can be established from the well-know law of Simon(17):

$$\Delta P = a \left[\left(1 + \frac{\Delta T}{T_0}\right)^b - 1 \right] \qquad (13)$$

where a and b are the Simon coefficients, the numerical values of which for many liquids are given in papers(17 and 18). The dependence of ΔP on ΔT can also be found from the Clapeyron-Clausius equation:

$$\frac{\Delta P}{\Delta T} = \frac{q_m}{T \Delta V} \tag{14}$$

where q_n is the specific melting point, T the melting point at a pressure P, and ΔV the difference between the specific volumes of the substance in liquid and solid states, respectively.

Thus, having determined T_{max} from (12) and substituted it in (13) or (14), one can find the value ΔP_{max}, which will correspond to the upper limit of sensitivity of the liquid to crystallisation on ions.

It is obvious that in more accurate thermodynamic calculations it is necessary to take into account the effect of the adiabatic variation of the temperature of the liquid due to the volume compressibility under the action of pulsed pressure.

The changed pressure on the liquid should be sustained for the time necessary for the crystalline nuclei to grow to a visible size (.1 mm). This time, from data on the speed of growth of the crystals(19) should be 10^{-4} - 10^{-2} sec, and the time of reversible solution upon re-establishment of the pressure on the liquid is 10^{-2} - 10^{-1} sec.

5. Example. Crystallisation on ions of rapidly super-cooled liquid argon.

To illustrate the propositions developed above let us estimate the possibility of the detection of ions in super-cooled liquid argon. Argon is selected because the full experimental data are available in the literature necessary for the application of formulae (11) and (14). The following data are used below:

$\varepsilon_1 = 1{,}5$ $\varepsilon_2 = 1{,}6$ $M = 39{,}9$ g/Mol; $\rho = 1{,}41$ g/cm^3

$\sigma = 2{,}1$ dyn cm^{-1}; $q_0 = 268$ cal/Mol; $T_0 = 83{,}8$°K; $a = 2114$, $b = 1{,}593$

The results of calculations according to formula (11) are presented in graphs in Fig. 1. The value of the super-cooling ΔT in degrees, is plotted against the radius of the equilibrium nucleus in angstroms. It can be seen from the figure that all the curves with $z \neq 0$ are below the curve of spontaneous nucleation of centres of crystallisation ($z = 0$). This fact points to the enhanced probability of the nucleation of crystalline particles on separate charges and charged complexes.

It follows both from an analysis of the curves and from formulae (12) and (13) that in order to render visible all the ions in liquid argon it is necessary to super-cool it to 9.5° ($\Delta P = 360$ atm). However, in charged complexes with $z \approx 3$ steady growth of crystals will occur when $\Delta T_{max} = 4.5°$ ($\Delta P_{max} = 150$ atm).

The investigations reported in this paper confirm the assumption of Bol'shanina and Kuznetsov as to the active influence of the charges on the speed of crystallisation of super-cooled liquids. The results obtained may serve as a basis for developing controlled liquid chambers.

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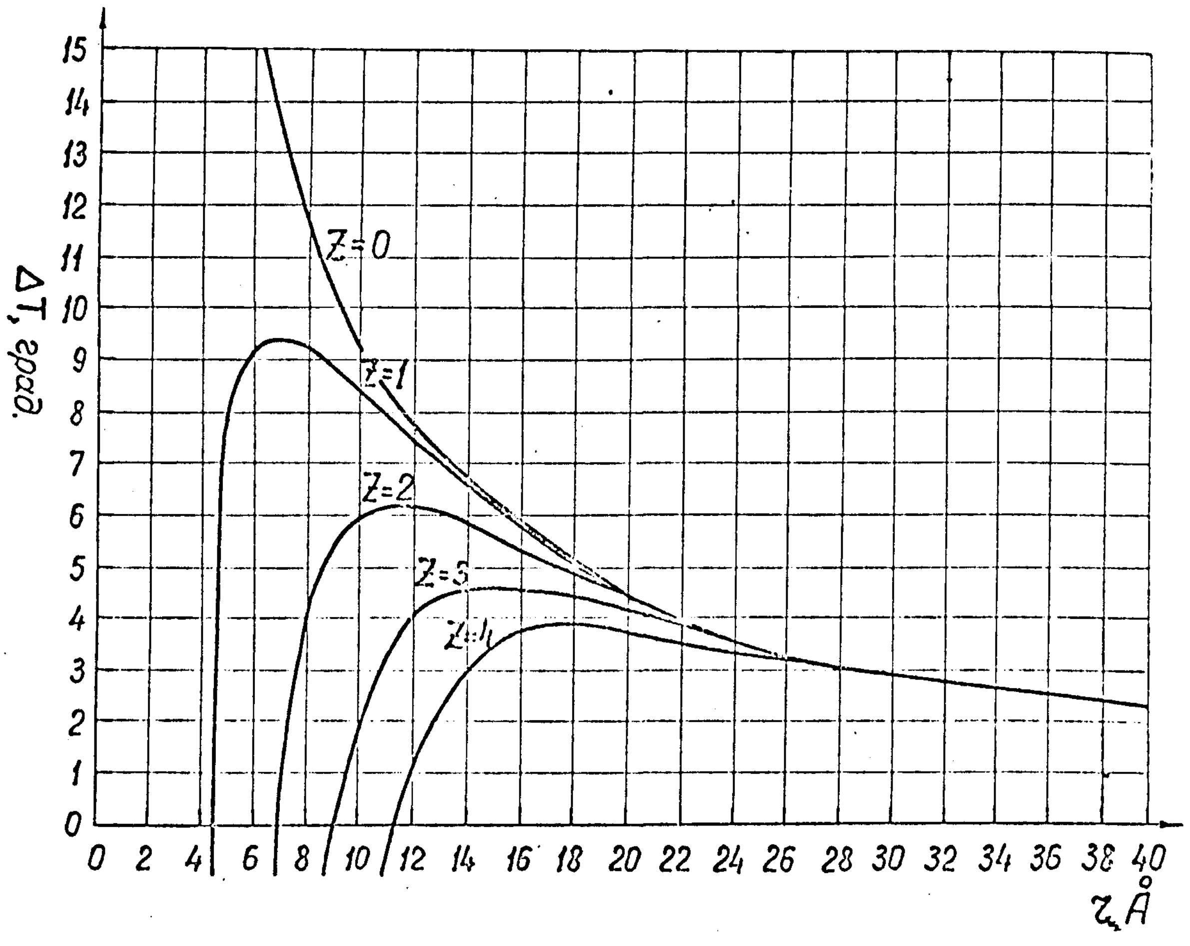

Fig. 1 Dependence of stable super-cooling of liquid argon on the radius of the nucleus and the value of the charge.