

11<sup>th</sup> IYPT '98  
solution to the problem no. 10  
presented by the team of RussiaII  
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**Repeated freezing**

While a vessel filled with an aqueous solution of a volatile fluid, e.g. ammonia, ethanol or acetone, is being cooled, repeated freezing and melting may be observed near the surface. Describe and explain the phenomenon.

**Overview**

- Experiments
- Explanation
  - Qualitatively
  - Self-oscillating systems
- Discussion of the differential equation
- Conclusion



## 1 Experiments

To study this phenomenon, we used an experimental set-up that involved a vessel filled by a snow-salt mixture and a test tube with the solution dipped into this vessel. Alternating freezing and melting were easily seen by the naked eye, and these effects were recorded by electronic filming. The snow-salt mixture causes the temperature to drop to  $-20^{\circ}\text{C}$ . Some time later, the solution in the test tube begins to freeze. Nuclei on the surface appear, then melt, then originate again, etc.

## 2 Explanation

### 2.1 Qualitatively

Qualitatively, this phenomenon can be explained as follows. Consider a vessel filled by an alcohol-water mixture. Let us assume that alcohol can evaporate into the surrounding ambient, where the alcohol concentration  $C_0 = 0$  (see figure 1).

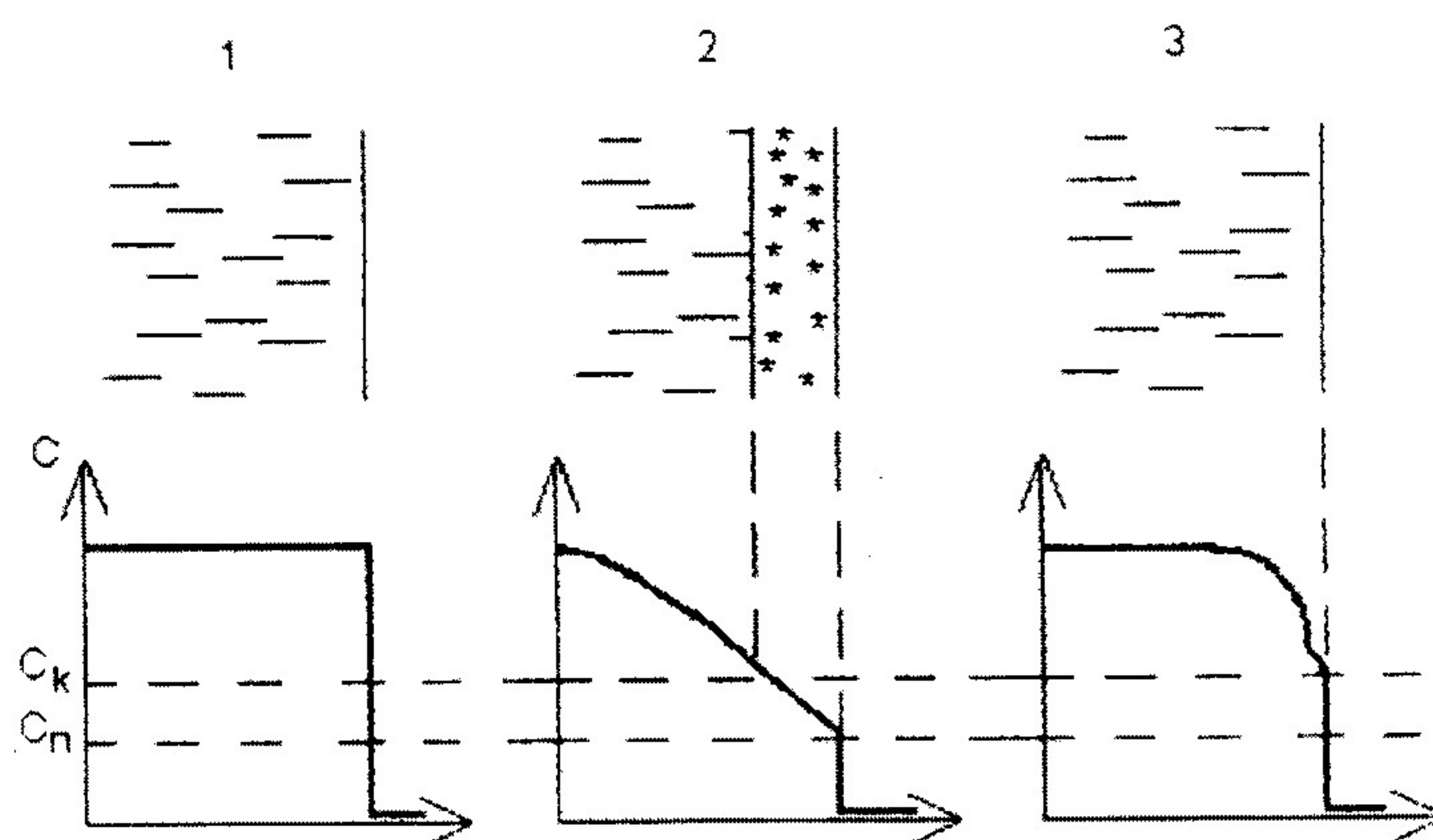


Figure 1: Assumed time variation of the solute concentration

Figure 1 (left) shows the assumed initial concentration of the solute in the solution. The volatile component is easier to evaporate from the water surface, its evaporation proceeding faster than its diffusion from the bulk to a thin near-surface layer. Since the freezing point of the solution increases with decreasing alcohol concentration, this layer begins to freeze at some concentration  $C_n$ . In figure 1 (middle) the assumed distribution of the solute concentration at the beginning of crystallisation is demonstrated. In our case, upon freezing the solution, water freezes, whereas alcohol evolves; in other words, the constituents are separated. Therefore, the alcohol concentration at the surface rises. Moreover, resulting pieces of ice inhibit alcohol evaporation, and the alcohol concentration increases further because of outward diffusion. An increase in the alcohol concentration to some value  $C_k$  leads to gradual ice melting, in which, in turn, results in alcohol evaporation from the surface layer, etc. The concentration curve for the solute in the solution at the instant of melting is shown in figure 1 (right).

Here, the philosophical LE CHATELIER principle, which states that a system tends to compensate any effect exerted on it, is quite obvious. Freezing increases the solute concentration in the solution. To compensate these increase, the ice melts and adds some amount of pure water to the system, thus decreasing the solute concentration.

### 2.2 Self-oscillating systems

This system refers to the class of self-oscillating systems. The thermal energy of the solution serves as an energy source. The ice that is produced on the surface acts as an energy controller. The solution itself is a self-oscillating system (oscillation of concentration). The processes that change the alcohol concentration in the near-surface layer perform the function of feedback.

Self-oscillation in solutions may be considered as a regular irreversible process that repeatedly occurs under the same macroscopic conditions. Self-oscillations do not require any external oscillating actions but arise from oscillating instabilities with their subsequent stabilisation due to (1)



the termination of energy delivery to the system and (2) energy dissipation (loss). Self-oscillating systems are inherently non-linear; otherwise, the oscillation amplitude would rise indefinitely. In our system, the oscillation is excited by the solute concentration fluctuations in the solution; in other words, our system is the one with a soft mode of oscillation excitation.

Let us consider the differential equation that describes the behaviour of our self-oscillating system:

$$a\ddot{x}(t) + b\dot{x}(t) + cx(t) = 0 \quad . \quad (1)$$

Where  $a$ ,  $b$ , and  $c$  are some coefficients;  $x$  is the variable concentration of the solution in the near-surface layer; and  $\dot{x}$  is the rate of concentration variation. This equation is similar to those that describe, for example, an RLC circuit or pendulum oscillation under friction. Here,  $a\ddot{x}$  stands for inertial forces (the presence of oscillation implies the presence of inertia);  $b\dot{x}$  refers to friction forces, which are responsible for the nonlinearity in the system; and  $cx$  designates an elastic restoring force. A solution is generally a system with distributed parameters, that is, each piece of ice may have its own oscillating frequency. While solving the equation, we assume that our system has lumped parameters.

Introduce the following designations:  $a = m$ ,  $b = 2m\gamma$ , and  $c = m\Omega^2$ . Then equation (1) may be represented in the form

$$\ddot{x}(t) + 2\gamma\dot{x}(t) + \Omega^2x(t) = 0 \quad . \quad (2)$$

### 3 Discussion of the differential equation

Let us trace the behaviour of the system in time. To do this, we shall solve equation (2). Define the initial conditions:

$$\begin{aligned} \ddot{x}(t) + 2\gamma\dot{x}(t) + \Omega^2x(t) &= 0 \\ x(0) &= x_0 \\ \dot{x}(0) &= 0 \end{aligned}$$

Now consider the case when  $\Omega^2 > \gamma^2$ ; that is, friction is weak. As friction, we may take a decrease

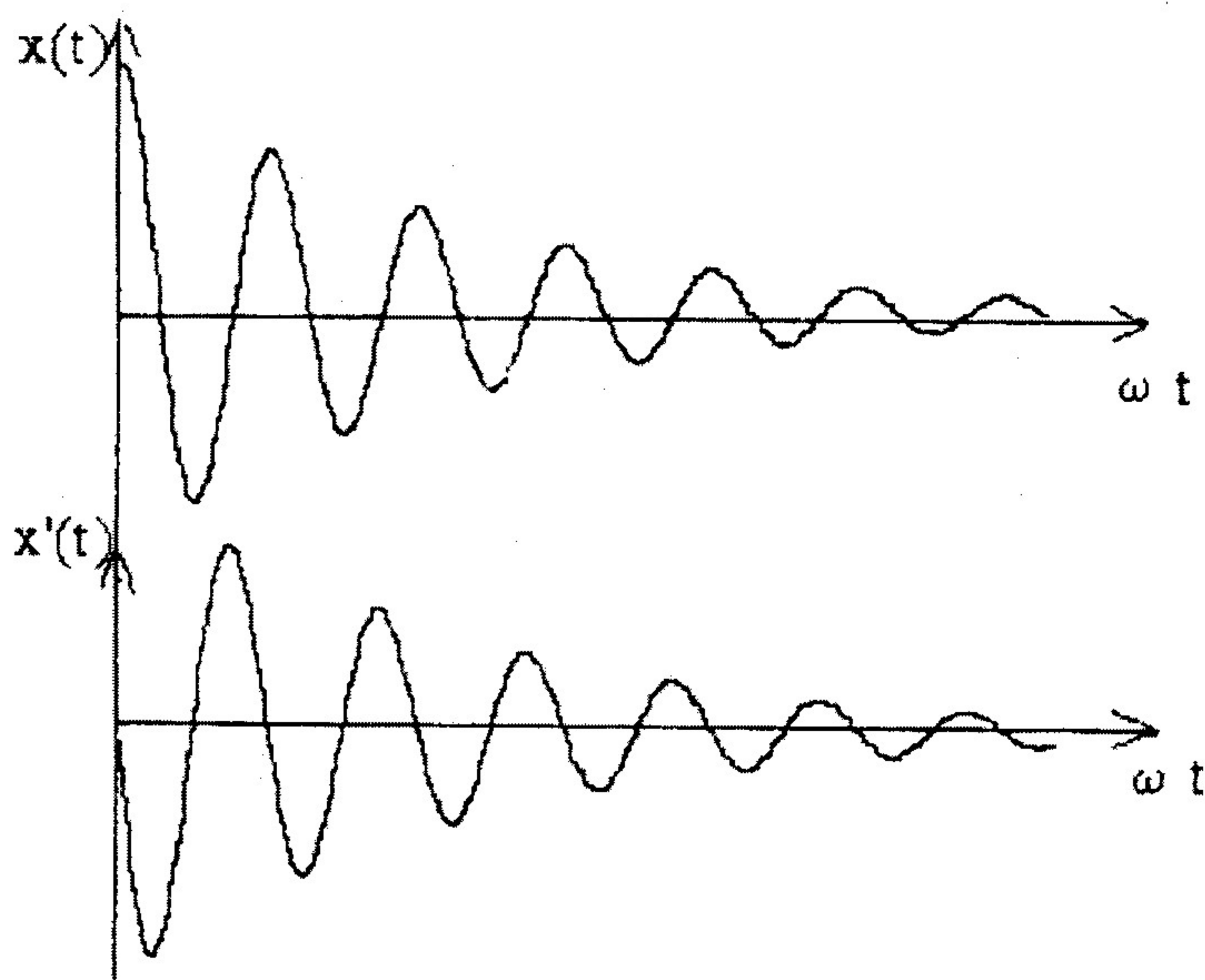


Figure 2: Derivation  $\Omega^2 < \omega^2$

in the solute concentration because of solute evaporation and a loss of the solution energy due to solution cooling.

Introduce the designations:  $\omega^2 = \sqrt{\Omega^2 - \gamma^2}$ ;  $\sin \varphi = \frac{\gamma}{\Omega}$ ;  $\cos \varphi = \frac{\omega}{\Omega}$ .

Then the solution of this equation is

$$x(t) = x_0 \frac{\Omega}{\omega} e^{-\gamma t} \cos(\omega t - \varphi) \quad (3)$$



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We take the first derivative of this equation

$$\dot{x}(t) = -x_0 \frac{\Omega^2}{\omega} e^{-\gamma t} \sin \omega t \quad (4)$$

The first derivative has the significance of the rate of solute concentration variation in the solution. For convenience, expressions (3) and (4) are displayed graphically (figure 2).

It is seen that the oscillations decay with time and eventually disappear.

If  $\Omega^2 < \omega^2$  (high friction), the behaviour of the system will be different. Equations that describe

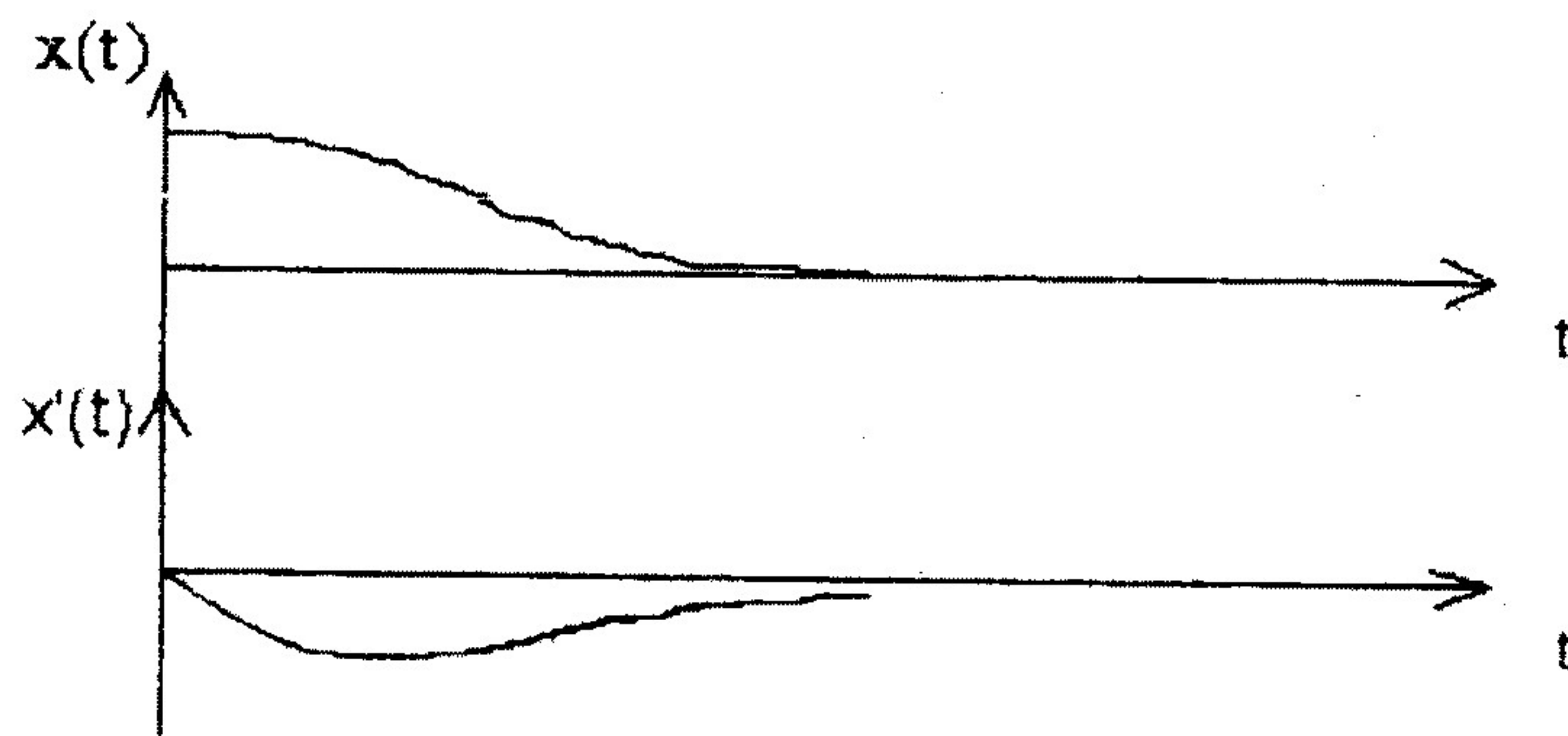


Figure 3: Derivation  $\Omega^2 > \omega^2$

the system behaviour in the case of high friction are rather complicated; so I shall restrict myself to purely qualitative analysis. In figure 3 that follows, one can see the time dependencies of the solute concentration and the rate of solute concentration variation. It is obvious that no oscillations will be observed in such a system.

The above solutions are obtained for the solute concentration variation. Note, however, that the development of ice nuclei is directly related to this process. Therefore, it would be reasonable to assume that the time variation of the ice nucleus size will follow the same dependencies.

This phenomenon was described by V. BURAVTSEV in 1983. Its model assumed that a nucleus is ball-shaped and occupies some unit volume, while a volatile substance diffuses into a vessel from some tank where the concentration  $C_0$  is constant and evaporates from a near-surface layer into an impurity-free space. Water freezes out from the solution; hence, it may be supposed that the ice does not contain alcohol. The impurity concentration in the vessel may be written as  $C = \frac{n}{1-V}$ , where  $V = \frac{4}{3}\pi R^3$  is the ice nucleus volume and  $n$  is the number of alcohol molecules in the vessel. Assuming that the evaporation is proportional to the ice-free part of the vessel, we can write the balance equation:

$$\dot{n} = k_1 \left( C_0 - \frac{n}{1-V} \right) - k_2 (1-s) \frac{n}{1-V} \quad (5)$$

where  $k_1$  is the diffusion coefficient,  $k_2$  is the evaporation coefficient, and  $s$  is the cross section of an ice nucleus.

The equation for the nucleus radius variation can be written in the ONSAGER form:

$$\dot{r} = -k \frac{d\Phi}{dr} \quad (6)$$

Where  $k$  is a phenomenological kinetic coefficient and  $\Phi$  is the GIBBS potential, which for dilute solutions is expressed as:

$$\Phi = \mu_l - \Delta\mu V + nT \left( 1n \frac{n}{1-V} - 1 \right) + \alpha n + \sigma S \quad (7)$$

Here,  $\mu_l$  is the chemical potential of pure water,  $\Delta\mu = \mu_l - \mu_s$  is the difference between the chemical potentials of pure water and ice,  $T$  is absolute temperature,  $\sigma$  is the surface tension,  $S$  is the surface area of a nucleus, and  $\alpha$  is some factor.



Putting  $K = 4\pi\Delta\mu k$ ,  $\beta = \frac{T}{\Delta\mu}$ , and  $q = \frac{2\sigma}{\Delta\mu}$ , we rearrange equations (5) and (6) in view of (7) as

$$\dot{n} = k_1 \left( C_0 - \frac{n}{1-V} \right) - k_2(1-S) \frac{n}{1-V} \quad (8)$$

$$\dot{r} = K \left( \left( 1 - \beta \frac{n}{1-V} \right) r - q \right) r \quad (9)$$

These equations describe the growth of an ice ball and the variation of the solute concentration in the near-surface layer. Considering free energies, one can find the stable and unstable states of the solution. However, the associated procedure is cumbersome; so I described only the growth of an ice ball and the variation of the solute concentration in the solution. This model has a number of disadvantages: for example, it considers only instabilities and does not touch possible oscillations in the system.

Such processes are frequently encountered in the nature. For example, similar analysis applies to the origination and death of blood cells, breathing control in the human organism, and many other processes. At present, this domain of investigation is fairly popular, and many articles on this subject are available.

## 4 Conclusion

In conclusion, I would like to report the results of the experiment that was performed at the very beginning of my study. The mixture of water and the volatile liquid was cooled in liquid nitrogen, and when nitrogen drops fell on the surface of the solution, which was 'hot' for liquid nitrogen, the fine effect was observed: The moisture around the drops was condensed, and a trace appeared behind the drops like that arising behind a plane flying at a great altitude. The same effect takes place when water drops fall on a red hot frying pan. Before this experiment was a success, five litres of nitrogen, one litre of alcohol, and half a litre of acetone had been spent.