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Dissolution of a heavy liquid droplet deposited onto free surface of unlike liquid solvent

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Dissolution dynamics and kinetics of a heavy liquid droplet deposited onto the free surface (or inserted at a certain depth under the surface) of a massive liquid solvent have been studied experimentally. As the solvent are selected distilled water, as well as concentrated solutions of sugar or common salt. As the soluble media were chosen the colored substances of different types (aniline ink, Indian ink, medical solutions of brilliant greenery or iodine), which allowed us to observe and register on the camera all the evolution stages of the heterogeneous system (a colored drop spreading in a transparent solvent) within the convective mixing regime. If the temperature of the solvent is high enough (T>40^{o}C), the convective mode is not realized, and the droplet is almost immediately dissolved into the homogeneous solution, at a low temperature (in our case it is room temperature of 18-20 ^{o}C), the spreading configuration is very complicated: after deposition on the surface, the droplet spreads over it, then in the central part of the spot appear one or several vertical channels (the number of channels depend on the size and mass of the initial droplet, as well as the dynamics of surface spreading which is controlled by the surface tension), along which the solution penetrates into the interior of the solvent. When penetrating the solvent, the channels begin branching and forming secondary flows, and so on, until the bottom of the cell is reached by initial droplet material. If a liquid stream is introduced to the solvent under pressure (we use injection from a syringe needle), a single well defined vertical channel is formed, but its head at some depth undergoes reflection with the formation of backward flows and complex spreading patterns in the upper volume of the solvent.

Keywords: dissolution hydrodynamics and kinetics, solubility, convective regime.

Динаміка та кінетика розчинення краплі важкої рідини, вміщеної на вільну поверхню (або на певну глибину під цю поверхню). В якості розчинників вибрані дистильована вода а також концентровані розчини цукру або солі. У якості речовини, що розчиняється, обрані забарвлені субстанції різних типів (анілінове чорнило, креслярська туш, медичні розчини зеленки або йоду), і це дозволяє нам спостерігати та реєструвати на камеру усі стадії еволюції гетерогенної системи (забарвлена крапля розповсюджується у прозорому розчиннику) в межах конвективного режиму змішування. Якщо температура розчинника достатньо висока (T>40^{o}C), конвективна мода не реалізується, і крапля практично моментально переходить в однорідний розчин, натомість як при низький температурі (у нашому випадку це є кімнатна температура 18-20^{o}C) конфігурації розповсюдження зовнішньої краплі є досить складними: після нанесення на поверхню розчинника крапля розтікається вздовж поверхні, після чого у центрі поверхневої плями з’являються декілька вертикальних каналів (число каналів залежить від розміру та маси початкової краплі, а також від динаміки поверхневого розтікання, що контролюється поверхневим натягом), вздовж яких концентрований розчин починає стікати у тіло розчинника. Проникаючи у тіло розчинника, канали починають формувати вторинні потоки з новими каналами, і так далі, доки матеріал первинної краплі не досягне дна посудини. Якщо рідка речовина введена у розчинник під тиском (ми вводили речовину через голку медичного шприца), формується єдиний, добре визначений вертикальний канал, але на певній глибині він зазнає відбиття завдяки впливу граничних вимог та формує зворотній потік зі складними фігурами розтікання у верхніх шарах розчинника.

Ключові слова: гідродинаміка та кінетика розчинення, розчинність, конвективний режим.

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This paper is written in memory of Professor Ya.E. Geguzin.

Introduction

Experimental studies of sintering mechanisms of dissimilar crystalline solids brought into contact on surfaces with different crystallographic indices and exposed at different temperature conditions have a highly significant place in the scientific heritage of Prof. Ya.E. Geguzin [1-4]. In fact, the case at hand is the mechanism of mutual dissolution of unlike solids, which occurs through a surface spreading of the components and mutual volume diffusion in the contact zone enriched by structure imperfections of the crystal lattice. In this sense, the process can be interpreted as a diffusion-dislocation flow (creep) of the contacting components, which in the promoted stages of the process can be described as mass exchange between two extremely viscous liquids. On a qualitative level, this phenomenon can also be considered as a spreading-dissolution of a foreign substance droplet deposited on the surface of a viscous liquid or a solid. Moreover, the dynamics of droplets was the subject of special interest of Ya.E. Geguzin, the droplet dynamics was a subject of special research described in his famous book [5].

In the present paper we study an analogous problem realized on a simple model of two dissimilar liquids, one of which has the form of an isolated colored droplet introduced onto a free surface of massive optically transparent liquid solvent. This setup allows us the direct real-time observation of the dissolution kinetics[1)]. Of course, the mutual solubility, the effective viscosity and the surface tension at the points of contact of the components in the present case turns out to be much smaller in comparison with similar parameters for solid crystalline systems, but the relaxation times in the liquid solution are acceptable in order to observe and real-time registering the evolution of the system in different regimes of the droplet penetration into the solvent.

Experimental results

Figure 1 shows the configuration of an aniline ink droplet within a few seconds after its dropping on the free surface of the solvent which is distilled water. The experiments were performed at room temperature. Just after deposition of the ink droplet to the water surface it begins spreading over the surface of the solvent under gravity forces and surface tension. As a result, from the spherical droplet a biconvex lens has been formed, with thickness decreases from the center to the edges. The spreading is due to the vertical pressure gradient within liquid droplet, which tends to flatten the droplet to minimize the pressure difference between the upper and the lower part of the lens, but complete flattening is impeded by the curvature of the edge contour of the lens in the cross-section, perpendicular to the water surface. The shape of the lens in its lower part (immersed in water) is maintained through balance of forces at the water-ink boundary. At a certain moment, this boundary loses its stability, and this breakdown occurs mainly in the central part of the lens, as can be seen in Figure 1. In this case, a thin vertical primary channel is formed, and the ink from the upper basin flows into bulk solvent, while it can be seen that a stream of unevenly "diluted" ink flows through the channel.

As the channel penetrates into the interior of the solvent, the pressure in the head of the channel $p = \rho g h$ increases (h is the coordinate of the head channel, measured from the surface of the solvent, and ρ is density of the solvent), and at a certain depth h_0 the channel advance will be blocked, after which begins the secondary spreading of ink coming through the channel from the upper pool. This secondary spreading occurs already near the horizontal plane $h = h_0$, which leads to the formation of two (as in Figure 1) or several (as in our other experiments) new vertical channels. As can be seen from Fig. 1, the secondary channels have an irregular structure due to thermal and pressure fluctuation within the ink solution. In addition, it can be seen from Fig. 1 that in heads of secondary channels begin to form droplets, which after a while will become centers a new stage of spreading.

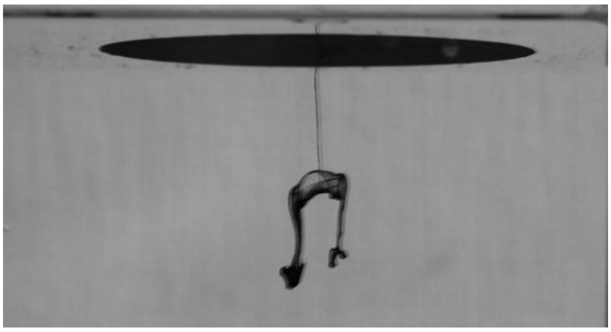
Fig. 1: Spreading and dissolving a droplet of aniline ink deposited to the surface of distilled water.

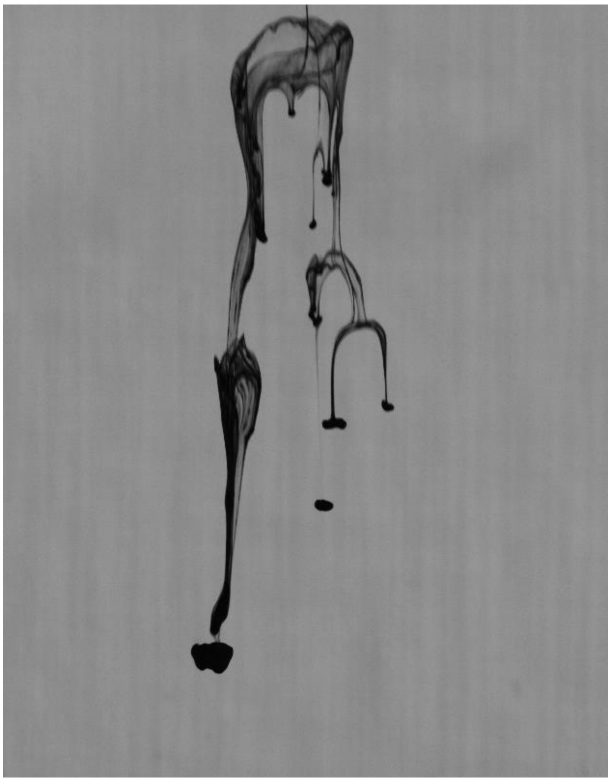
Fig. 2: Multistage spreading-dissolution of an aniline ink droplets penetrating beneath the surface of the solvent.

The multi-stage flow is illustrated in Figure 2, which shows how the run of a channel is stopped at a certain depth, and a new drop begins to form in the head of the stopped jet, which is similar to the formation of the drop at the end of the syringe needle, from which a viscous

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[1)] This problem was announced in the Problem List of International Physicists Tournaments 2018 (MFTI, Dolgoprudny, Moscow region). Experimental results were obtained by O. Yu. Zaitseva and discussed in her report presented at the IPT 2018.

liquid is released. Thus, the development of a vertical channel can be regarded as the introduction of a viscous liquid under the surface of the solvent (special experiments of this kind were carried out by means of liquid injection from a syringe, the needle of which sank to a certain depth, but in view of the limited volume of the paper we do not discuss here the corresponding results). The droplet at the end of the stopped channel grows because the flow of liquid from the upper reservoir continues along the channel, and as a result, the secondary drop spreads underwater, with the formation of new secondary channels, The created substance penetrates deeper and deeper into the solvent until it reaches the bottom of the cell, after which the progress of the moving vertical channel stops.

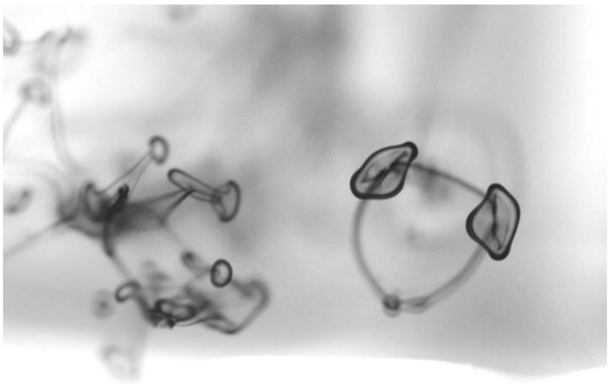

Fig. 3: Formation of ring structures when the drop is spreading under the surface of the solvent (top view to the surface solvent, the camera is focused on rings that are below the level of the primary subsurface spreading).

Extremely interesting is the process of the secondary spreading below the surface after the channel stop. The droplet formed in the head of the stopped channel continues to receive a dissolving substance, and from Figures 1 and 2 it is seen that the concentration of the colored liquid in the secondary droplets is higher than in associated channels, that is, the dissolved substance accumulates in the channel head, which leads to eventually secondary spreading. Figure 3 shows the configuration of the spreading subsurface droplets recorded by the camera on the side of the top of the solvent (the camera is focused so as to clearly record the process at the depth of secondary spreading). It can be seen that the secondary distribution of the flow occurs by forming rings unevenly filled with a solute, and already from these rings are nucleated the secondary channels through which the solution continues to flow down to the bottom of the vessel. The tendency to form ring structures during underwater spreading takes place because the droplet introduced at the determined depth is under a concentrated load from the upper column of solution, which crushes the drop from the center to the edges, and this process is restricted by the surface tension at the boundary between the droplet and the solvent. In the common sense, the droplet is profitable to accept the configuration of its outer surface in contact with the solvent, which would have as large as possible curvature with maintaining the maximal volume of the substance, for which it is difficult to form a homogeneous molecular solution with a concentration exceeding a certain thermodynamically equilibrate value of solubility (thermodynamically determined for the given temperature and pressure). In the thermodynamics of solutions, this effect is known as a limited solubility [7.8], which leads to the decay of both liquid and solid solutions where the concentration of components exceeds the limit of solubility. This process directly is associated with the mechanism of secondary phase nucleation during phase transitions of the first kind or the formation of precipitates upon the decomposition of solid mixtures. In our case, a subsurface droplet takes configuration of the torus (Figure 3), which allows to retain a significant amount of undissolved matter in a region restricted by a surface of large curvature. The curvature of the torus surface,

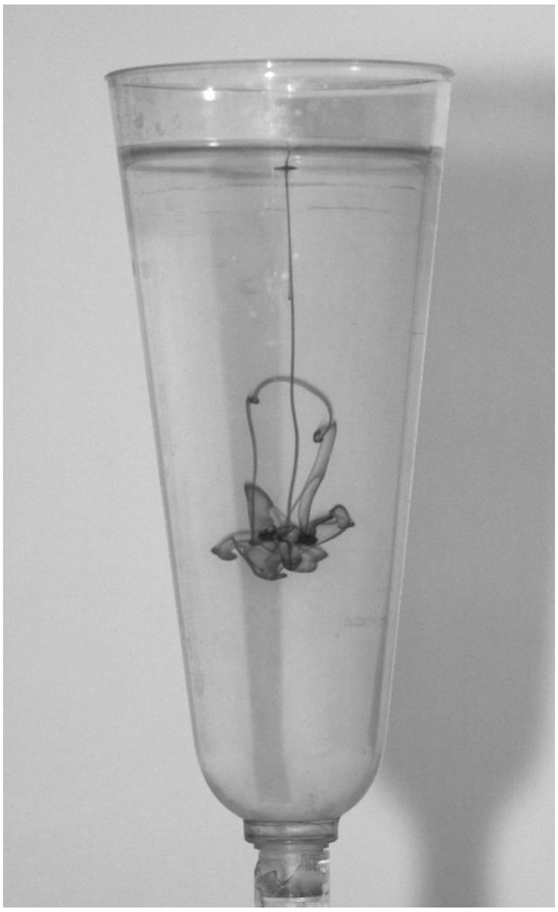

Fig. 4: Spillage outlet resulting from the introduction of a jet of ink at a high initial speed into the solvent.

however, can not be arbitrarily large, since the transition (evaporation) of precipitate molecules to the solvent is more simple from a curved surface, and this process is controlled by the equilibrium conditions with respect to pressures and chemical potentials on the boundary between the contacting phases. The shift of this equilibrium leads to a diffusive redistribution of the solution components between the contacting phases. In our case, the observed dissolution process is essentially nonequilibrate, under the determining control of the hydrodynamic (convective) regime in the gravitation field. Diffusion is activated at all stages of the process, but convective motions are predominant at the initial stage of dissolution at all temperatures of our experiments.

It can be seeing in the upper part of Figure 1, that there is a separation of the "tails" from the edge of the liquid spot on the solvent surface. This is a process of two-dimensional surface dissolution of precipitate which can be interpreted as surface diffusion of an external substance introduced into the solvent. Fluid penetrated into the solvent through channels, partially diffuses through the channel boundary, but it can be seen that the channels have very small diameter, which is the result of the same tendency to limit the distribution of concentric-bath solution with a large curvature surface to support the spatial stratification between liquid phases of different concentrations in a spatially inhomogeneous system.

And, finally, we present the result of another experiment (Figure 4), which refers to the jet of ink, put under the surface of the solvent from the syringe needle with high pressure and, therefore, with a high initial velocity. It is quite obvious that in this case we could expect the propagation of a well-defined flow of the injected liquid, because in this case the motion is purely hydrodynamic (diffusion characteristic times are large in comparison with the time of development of the hydrodynamic pattern). In principle, one would expect that a jet without essential destruction will reach the bottom of the vessel and, reflecting from its bottom will go in the opposite direction. However, as can be seen from Fig. 4, reflection occurs far from the bottom in the solvent, with the formation of secondary localized reflected jets, and with complicated scattering of the most part of the primary stream. It is important to note that the lower level of the reflection is strictly determined, and below this reflection boundary the solvent remains absolutely transparent. The reflection effect is due to the fact that the hydrodynamics of the primary jet stimulates the hydrodynamic motion of the entire system as a whole, and that is, the velocity field in the jet has been associated with the velocity field in the solvent by the boundary conditions on the boundary layer between the primary jet and bulk solvent (and the same reason holds true for the pressure field, as well as to the thermo-dynamic relations in a heterogeneous system). This means that the jet feels the presence of the boundary conditions on the walls and bottom of the vessel (in addition to everything, in our case the vessel has the shape of a cone, which, of course, complicates the problem) at each moment, and the normal components of the stream velocities at the bottom of the vessel are strictly equal to zero. Thus, the streamlines themselves are wrapped into the volume of the vessel. Reflection of the primary jet occurs then, when this jet enters the region of the reverse flow of the whole system, generated by the boundary conditions on the bottom of the vessel.

Discussion

The phenomenon studied in the present paper is a direct analog of the processes of mutual dissolution (mixing) of solids observed during the sintering in crystals brought into contact with their surfaces and placed in the conditions necessary for an active microscopic mass diffusion between these bodies (the diffusion is going both on the surface and in the volume of the crystals). In our case, the experiment is performed on dissimilar liquids, and therefore purely diffusive dissolution is complicated here by obvious hydrodynamic movements in a highly inhomogeneous liquid media. The macroscopic inhomogeneities are well-defined regions of the colored solution with evidently different concentrations of the components. In a sense, this picture resembles the evolution of decay in solid solutions. However, the solid solutions after disintegration are stable heterophase structure (that is, equilibrium at given temperature and pressure), while in our case of mixing liquids this "quasi-heterophase" structure remains metastable and evolves slowly to the state of a homogeneous solution. Of course, as the temperature increases, homogenization occurs faster, and in a solvent with a temperature above 50-60°C, the formation of the structures described above is impossible because the droplet introduced into the hot solvent decays immediately, and after one or two minutes, the state of a homogeneous solution is established. For this reason the experiments described above were performed on cold components (at temperatures of 10-20°C), and only in these conditions a steady reproduction of the pictures shown in Figures 1-4 is possible. Hydrodynamic regime of the initial stage of dissolution in liquid components with formation of channels can be associated qualitatively with the stage of active mass transfer in the developed diffusion zone of solids [4] , where the mutual diffusion leads to appearance of internal stresses and formation of a large number of crystal lattice defects facilitating the diffusion transfer. Strictly speaking, a strongly distorted crystal is no longer to be interpreted as a proper crystal, but it can be regarded as a viscous continuum deformed within hydrodynamic regime.

The question, however, is of how the surface contact breakdown occurs with the formation of the primary stream that flows into the solvent inside a narrow channel. The reason for this phenomenon is that the substance of a heavy liquid droplet deposited on the surface begins to diffuse in the solvent immediately after its application to the surface, and traces from this diffusion can be seen in Fig. 1. In addition, in Fig. 1 we can see that from the edge of the surface spot some ‘tails’ are torn off, and the matter spreads along the surface of the solvent. Thus, this is a quite obvious analog of surface diffusion observed at sintering in solids [1-4]. In our case, a droplet of heavy liquid, deposited on the surface of the solvent, forms on this surface a hole, in the center of which the pressing on the surface will be higher than at the edges of the lens [5]. This results that at the center of the spot the drop-solvent boundary will be destroyed, and the ink begins flow into the bulk solvent simply in the form of a localized jet in the usual hydrodynamic regime. The dynamics of a flooded jet is considered, for example, in the book of Landau and Lifshitz [6], but there was investigated only the case when a thin jet of a viscous liquid under pressure is injected into the volume of a complementary liquid with the same density and viscosity.

In our case, the situation seems to be much more complicated, since of mixing the heterogeneous fluids, and therefore it is necessary to describe hydrodynamics of an inhomogeneous medium with regard to the kinetics of mutual dissolution of components with limited mutual solubility. The jet penetrated under the surface flows into the solvent under the gravity forces, and its shape has the form of a cylindrical channel. This shape is supported by surface tension forces on the ink-solvent interface, and also the strength of Archimedes prevents its penetration into the bulk of the solvent. In this case, the movement of the jet head becomes slower, and the leakage of ink from the upper reservoir results in the formation of a bubble at the tip of the stopped jet. The jet stopped at some depth, continuing to grow, but in the form of a secondary lens that grows at a certain depth, eventually forming rings (Figure 3) due to the deformation of the secondary bubbles in a vertical pressure gradient. The ring is a jet curled into a torus, which allows to minimize the influence of the vertical gradient on the unlike liquid bubble introduced into the solvent. The surface of the torus has two principal radii of curvature, essentially different in magnitude: this is, firstly, a large radius of curvature (small curvature) along the generator of the ring and, secondly, a small radius of curvature (large curvature) in the cross-section of the torus.

The curvature of the jet surface has a special significance in our case. On the one hand, under the curved surface on the jet acts the surface tension force, which helps to support its shape. On the other hand, from a curved surface an atom can be easily "evaporated" into the bulk solvent. Thermodynamics of this process is completely analogous to the coalescence of second-phase nuclei in dispersion-hardening alloys or coalescence of pores in crystals [1-4,7]. Thus, the flooding of a vertical jet is a complex process of propagation of a hydrodynamic flow, which at the same time dissolves in the volume of the solvent medium due to both diffusion and branching of the secondary flows. This process is a direct analogy of the formation of ‘trees’ in separated solid solutions with a small coordination number of the interaction in the mixture [8,9]. As an example can also be given the phase separation of dilute solid solutions of helium isotopes (^{3}He-^{4}He) which, in view of the quantum nature of the interatomic interaction in these systems, undergo decay at any arbitrarily small concentration of the impurity component in solution, so that the coordination number (the number of nearest neighbors) in the second phase does not exceed several units [10-12].

Conclusion

It seems that the problem we are considering here has only purely academic interest, but we can indicate one area where the results can probable find a practical application. The classical problem of heterogeneous mixing is the problem of evolution of oil spots on the water surface, arising from the spillage of oil (or other process fluids) due to accidents in transport or production. Of course, this problem is also interesting from the point of view of direct behavior of model complex heterophase system in the hydrodynamic regime.

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