

On the Geometric Formalism of Thermodynamics: In the Context of Liquid Bubble-Boiling and Matter Glassy State

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ABSTRACT

Modelling of fluids vertical convection in nature by means of our original bubble-boiling method (BBM) allowed us to investigate behavior of the thermodynamic parameters of solutions during the whole process of heating (result of joint action of the processes of temperature conductivity, thermals and vapour bubbles mixing convective motion). There were obtained the universal dependence between the of bubble-boiling temperature and density of the solutions and existence of linear laws between points of discontinuities: T_{dc} , t_{dc} , S_{dc} , and ρ_{dc} which we can write, for $q = \text{const.}$, as: $(dT/d\rho)_{dc} = \text{const.}$, $(dp/dt)_{dc} = \text{const.}$, and $(dS/dT)_{dc} = \text{const.}$ This method allowed us to show experimentally a similarity between the temperature-time (T, t)-diagrams of some matters water solutions and Tammann's glassy state-diagrams. We try to find accordance between well-known Euler's theorem on right polyhedrons and Gibbs thermodynamic rule about heterogeneous systems. Perhaps, using Gibbs-Tammann method for description of multicomponent system ($n = 4, 5, \dots$), may obtain tetrahedron, octahedron and others. Then, for precise establishment of the moments of the liquids the micro- and macro-scale bubble-boiling regimes beginning, we analyzed our experimental (T, t)-, $(dT/dt, T)$ -, and $(d^2 T/dt^2, T)$ -curves, which showed the existence of the acute maximums near temperatures $T = 40^\circ\text{C}$ and $T = 80^\circ\text{C}$, respectively. Naturally, the same picture shows the temperature dependence of following even derivative of T with respect to t . Thus, this method of processing of $T(t)$ -experimental data allowed us to avoid use of complex high-speed filming technique. Obtained analogy between thermodynamic diagrams of the glassy state of matter and the bubble boiling of liquids is caused by the fluidity of the glass as liquid (that is, "glass is liquid" (Tammann); undoubtedly, this is the best example of the phenomenon supporting well-known Frenkel's kinetic theory of liquids). More over one can assume that the idea of the kinetic theory was "prompted" to Frenkel by Tammann's glassy state, as probably form of Gibbs rule was "prompted" to him by Euler theorem about polyhedrons.

Key words: thermodynamic state, homogeneous, heterogeneous, spherulite, glassy state, bubble-boiling method, Gibbs' rule, Tammann's diagrams, Euler's theorem, polyhedrons.

1. Introduction

Some years ago the authors suggested new fluids bubble boiling method for modeling (BBM) of vertical convection processes having place in the geospheres. Then they were developed in our recent articles for artificial solutions and analyzed by means of $T(t)$, $\Delta S(T)$, and $T(\rho)$ experimental curves for definition of admixture of the mass content density of solutions or natural waters. There were obtained optimal values of the liquid volume, the heating intensity, and temperature measurement frequency. BBM-method allows us for short time to determine main thermodynamic parameters, to avoid the technical difficulties of preparation, and carry out measuring, especially near the points of the second kind of discontinuity in the temperature interval $40^\circ\text{C} - 80^\circ\text{C}$ between the micro- and macro-bubble boiling regimes [7-12]. For more precise determination of the second kind of discontinuity of the temperature of heating liquids in time except of time dependence of the classical entropy ($dS = dQ/T$ °K, t) there were constructed time dependence of pseudo-entropy ($d\Sigma = dQ'/T$ °C, t), where instead of Kelvin's degree °K of temperature was used Celsius, °C, one. By this way it was discovered the point of discontinuity at T near 40°C which was not seen in case of the curve ($dS = dQ/T$ °K, t). Therefore then it was recommended to use pseudo-entropy ($d\Sigma = dQ'/T$ °C, t) at ($40^\circ\text{C} < T < 50^\circ\text{C}$). Below it is considered: (a) similarity between experimental (T, t)-curves of any matter water solutions and according diagrams of the matter glassy state; (b) the peculiarities of mentioned (T, t)-

curves at the points of discontinuities (40 °C and 80 °C) by means of applying the calculus method to the points of contrary flexure (liquid micro- and macroscale bubble-boiling regimes beginning, respectively) on the curves (dT/dt, T). It is also discussed accordance between well-known Euler's theorem about polyhedrons, Gibbs thermodynamic law and Tammann-Frenkel view on the similarity of solid and liquid bodies structure.

2. Thermodynamics of Gibbs-Tammann and Euler's polyhedron [1-3, 6]

2.1. Geometrical formalism of thermodynamics

As necessary, the classic sciences consider ideal model of their objects of investigation: mathematics – right geometric figures, mineralogy– crystal polyhedron, physics and chemistry – ideal gases and liquids, geophysics– crystals, which play paramount role, in particular, on close examination of pieces of volcanic glass and the Earth's interior generally. Therefore, study of a thermodynamics of the matter phase transformation in nature and in a laboratory usually is provided on the basis of correlation between a form of crystal and its configuration energy. In this connection it is interesting to pay attention to the well-known expressions – thermodynamic rule of Gibbs [1], and geometric formula of Euler [6].

On the one hand, when a chemical homogeneous substance is appeared in two or three aggregate states simultaneously under invariable pressure and temperature, then they are in equilibrium with each other and submitted to the following Gibbs rule of phases:

$$F = N + 2 - R, \quad (1)$$

Where F is a degree of freedom, N is a number of matters, and R is a number of phases.

On the other hand, Euler's formula for relation between the geometric characteristics of a polyhedron is following:

$$F = E + 2 - V, \quad (2)$$

where F is a number of faces, E is a number of edges, and V is a number of vertexes.

In formal comparison of these expressions it is arisen an instant a neo us impression that they are similar not only outwardly. They also reflect dependence between them: between thermodynamic parameters of the system and its inner structure, exactly – crystal structure or in case of Euler's geometric formula –the polyhedron. Both of them characterize the stable state of the systems.

As is well known, a “transition of non-isotropic state into other one is impossible, as a transition of isotropic state into non-isotropic one is impossible”. In view of this property of crystals, I think that it is possible to find among of many-component systems corresponding sample one. Analysis shoes that such object is the four-component (n = 4) system. For n ≤ 3 Tammann uses plane geometry, for n ≥ 4 his thermodynamic diagram is projected in space geometry, in particular, in the form of tetrahedron (n = 4). More detail this question will be discuss below.

2.2. The stable and unstable stations of melting and bubble boiling thermodynamic systems

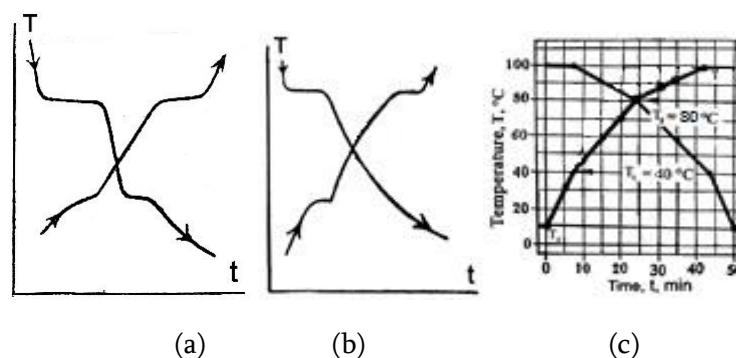


Fig. 1. Temperature-time (T, t)-diagrams of heating and cooling of some matters:(a), (b) –Tammann's qualitative curves are (T, t)-diagrams of according processes [3]; (c)– (T, t)-experimental curves of saturated solution for any matters (using [11,12]).

Analyse of Fig. 1 shows that at the points of phase-transformations crystal-liquid and vice-versa (Fig. 1a, b) the angle of refraction is larger than at the change of micro- and macro-bubble boiling at heating and cooling (Fig. 1c), respectively. It is necessary to note, that the brunch of the cooling curve in Fig. 1c, is the dashed curve in Fig. 2b. Full time of cooling is 184 min (not 40 min as in the diagram of Fig. 1c), then real curve in the last case would have view as the cooling curves in diagrams of Fig. 1a, b, respectively. Above mentioned similarity of the diagrams allow us to speak about the short-range ordering considered thermodynamic systems. This moment is confirmed by investigations [2] according which “molecules are more active in a glass than in a crystal: in crystal lattice molecules are more ordered, and in a glass they are settled down chaotically.” Thus, in that case the glass is supersaturated liquid. It is interesting other citation: three isotropic states: gaseous, liquid and solid (glassy) can transform from one state into another one without division on two phases (persistently). Quite otherwise the things are in case of crystal – non isotropic phase – generation from a vapour, liquid or glass [2]. That is, above mentioned likeness of diagrams allows us to speak about of short-range order in the considered substances. From the point of view both of physics and mathematics, the order-disorder phenomena and superlattice alloys demand special consideration, firstly proofed by Tammann experimentally which further were developed in [13-17] and others.

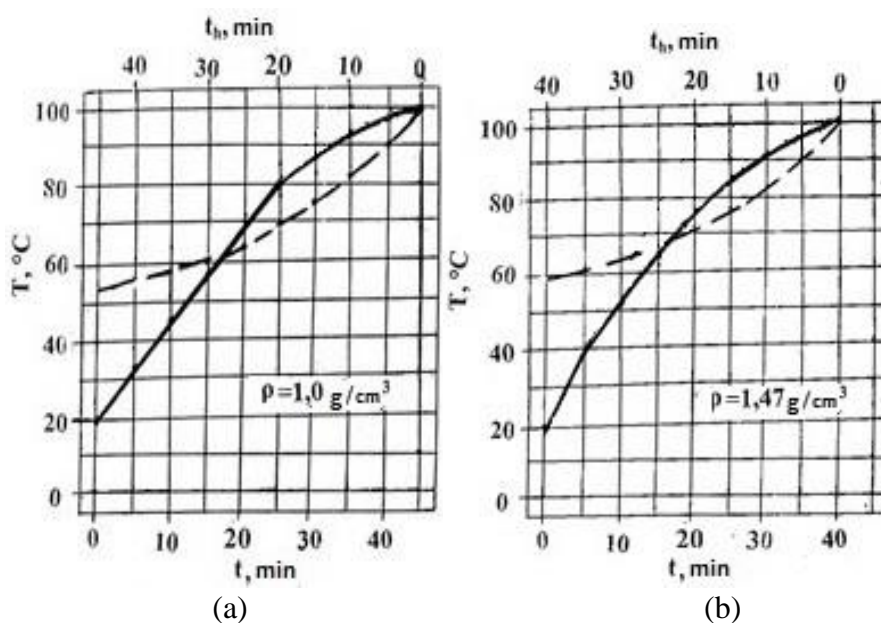


Fig. 2. The hysteresis curves of: (a) – pure water ($\rho = 1 \text{ g/cm}^3$) and (b) – sugar solution in a water ($\rho = 1.47 \text{ g/cm}^3$) when the intensity of heating $q = 2 \text{ W/cm}^2$; the solid lines correspond to the heating process of liquids (time scale is below), and dashed lines – to the cooling of them (time scale – above). Time of cooling of pure water was equal to 136 min, in case of the sugar solution – 184 min.

Fig. 2 shows the results of detail measuring during heating from initial temperature $T_0 = 20^\circ\text{C}$ to the intensive bubble boiling temperature $T_3 = 100^\circ\text{C}$ and then reverse motion of both curves (H_2O and $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ solution of maximal density, $\rho = 1.47 \text{ g}\cdot\text{cm}^{-3}$). There are two points of crossing curves at temperature $T_3 = 100^\circ\text{C}$ and lower at $T_2 \approx 62^\circ\text{C}$. In case of clear water, H_2O , time of heating from 20°C to 100°C equals to 45 min; coordinates of the second kind discontinuity are following $T_1(80^\circ\text{C}, 25 \text{ min})$; coordinates of point of boiling are $T_3(100^\circ\text{C}, 45 \text{ min})$. In case of sugar, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, time of heating from 20°C to 100°C equals to 40 min; coordinates of the second kind discontinuity are following $T_2(40^\circ\text{C}, 5 \text{ min})$; coordinates of point of boiling are – $T_3(100^\circ\text{C}, 40 \text{ min})$.

Unlike the water solution of NaCl (with maximal density $\rho = 1.2 \text{ g cm}^{-3}$, and temperature of boiling $T_3 \approx 108^\circ\text{C}$), in case of sugar water solution ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$), a rise of boiling temperature doesn't occur, and its

boiling temperature was equal to $T_3 = 100^\circ\text{C}$. In case of sugar water solution of maximal density ($\rho = 1.47 \text{ g}\cdot\text{cm}^{-3}$), the hysteresis square between solid line and dashed one, directed in the opposite direction (of low cooling process of the solution from the point of boiling $T_3 = 100^\circ\text{C}$) before their crossing with each other equals to, respectively: (a) for clear water ($\rho = 1.0 \text{ g}\cdot\text{cm}^{-3}$) the hysteresis square $\Delta D_h(\text{H}_2\text{O}) \approx 3.5 \text{ un.}$ coordinates of this point are following: $T_h \approx 62^\circ\text{C}$, and corresponding time of cooling, $t_h = 28 \text{ min}$; for sugar solution of maximal density $\rho = 1.47 \text{ g}\cdot\text{cm}^{-3}$, $\Delta D_h(\text{C}_{12}\text{P}_{22}\text{O}_{11}) \approx 2 \text{ un. sq.}$; coordinates of this point are following: $T_h = 68^\circ\text{C}$, and corresponding time of cooling, $t_h = 23 \text{ min}$; ratio between hysteresis squares of sugar and clear water equals to $\approx 4:7$. Time of cooling of pure water was equal to $136 \text{ min} = 2 \text{ h } 16 \text{ min}$, and in case of the sugar water solution was equal to $184 \text{ min} = 3 \text{ h } 04 \text{ min}$. (Fig. 2).

Fig. 3 represents results of the experimental investigation of temperature change in time of saturation solution of any organic or nonorganic matters in a beaker of water (as usually, in our early experiments [7-12]). Analysis of the $(dT/dt, t)$ -curve of the liquid temperature growth rates shows the points of discontinuities (tangent dashed lines: 1, 2, 3, 4, 5) and the point of inflection between points 3 and 4 at $T = 40^\circ\text{C}$ (on the $T(t)$ -curve showed to the right of arrow). As this was to be expected, there the curve of $(d^2T/dt^2, t)$ has extremum at the point between the micro- and macro-scale bubble boiling regimes of liquids [11, 12]. The availability of the point of inflection (T_w) was shown by Tammann [2] for dependence of the second order differential of the glasses physical properties on the temperature curves. The point T_w is in the temperature interval of softening of the glass (T_f, T_g), where T_f is the temperature of the glass transformation into liquid under slow heating; T_g is the temperature at which the body is become fragile under cooling, but not at once [2].

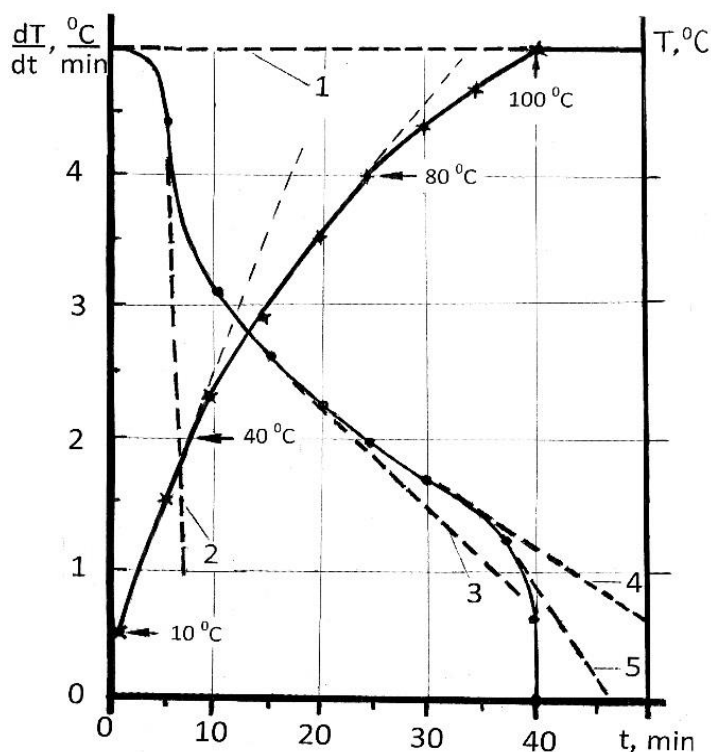


Fig.3. $(dT/dt, t)$ -curve shows the rate of liquid temperature growth against the time, T (the curve joins points: ●); and (T, t) -curve shows the liquid temperature against the time, t (the curve joins points: x).

For making more precise of the moments of the liquids bubble-boiling micro- and macro-scale regimes appearances, respectively at $T = 40^\circ\text{C}$ and $T = 80^\circ\text{C}$, we also constructed the curve $(d^2T/dt^2, T)$ (Fig. 4.). Here we see as both points of contrary flexure at the values of temperature $T = 40^\circ\text{C}$ and $T = 80^\circ\text{C}$

(the curve $(dT/dt, T)$) are illustrated by means of two acute maximums (!) of the curve $(d^2T/dt^2, T)$). As this was to be expected, the availability of these maximums near $40\text{ }^\circ\text{C}$ and $T = 80\text{ }^\circ\text{C}$ was not accident.

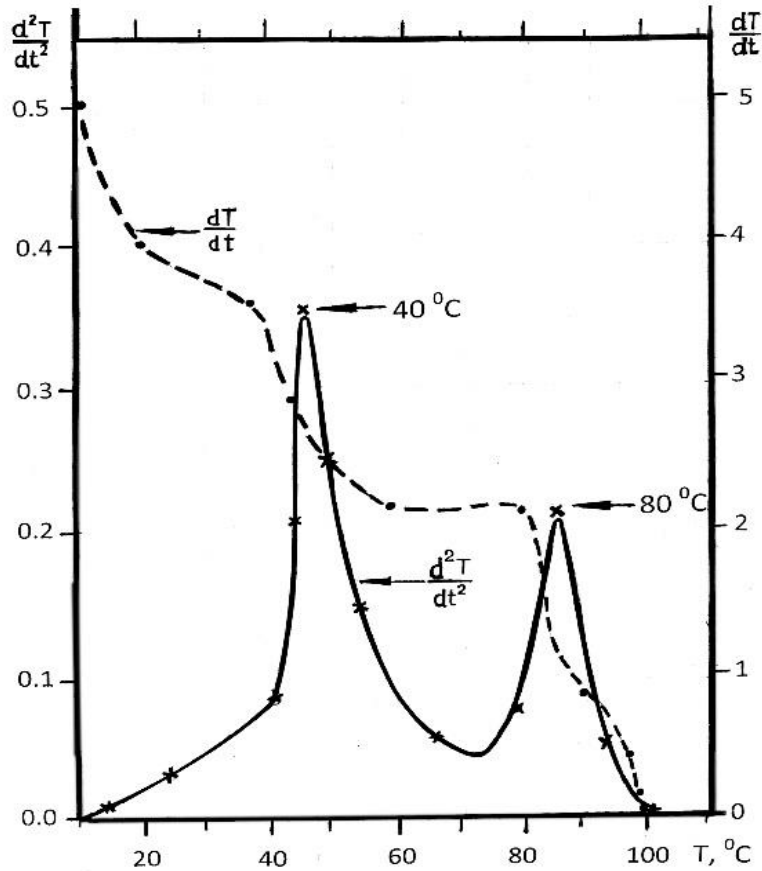


Fig. 4. $(dT/dt, T)$ -curve shows the rate of the liquid temperature growth against the temperature, T , (the curve joins points: \bullet); and $(d^2T/dt^2, T)$ -curve shows the liquid temperature growth acceleration against the temperature (the curve joins points: \times).

As it is seen, the experimental curves of Fig. 3 and Fig. 4 are in a good accordance with each other and with Fig. 1a, b give additional new information about similarity of considered here heating and bubble-boiling process of liquids and peculiarities of glassy state-crystallization processes (Fig. 1c) [2, 3].

3. Analysis and discussion.

3.1. Analyze of Fig. 1 shows that at the points of phase-transformations crystal-liquid and vice-versa (Fig. 1a, b) the angle of refraction is larger than at the change of micro- and macro-bubble boiling at heating and cooling (Fig. 1c), respectively. Difference between (T, t) -crystal heating-cooling diagrams (Fig. 1a, b) and according curves of any matter saturated solution (Fig. 1c) takes place as crystal's heat conduction is larger than the liquid's one. Though the results of different processes are discussed here (process of glass formation on the one hand and the bubble boiling on the other hand), it would be interesting to compare the spherulites and the vapour bubbles concentration with micro- and macro-scale spectrums of water pulverization and with air bubbles formation in the liquid phase during freezing of the super-cooled water (or ice melting) in front of the moving front of the solid phase.

According results are represented below in Fig. 4. For making more precise of the moments of the liquids bubble-boiling micro- and macro-scale regimes appearances it was used $(d^2T/dt^2, T)$ -function, which (and every even derivative of T with respect to t) has an acute maximum. For example, the curve $(d^4T/dt^4, T)$ is narrower and lower than the curve of $(d^2T/dt^2, T)$: near 40 °C approximately ten times and near 80 °C twenty times, respectively. Therefore, one may conclude that precise measuring of temperature $T(t)$ is enough for exact definition of the bubble-boiling micro- and macro-scale regimes beginnings moments (without of high-speed filming technique).

As we see, the experimental curves of Fig. 3 and Fig. 4 are in a good accordance with each other and with Fig. 1a, b) [2, 3]. They give new additional information about similarity of considered here heating and bubble-boiling process of liquids and peculiarities of glassy state-crystallization processes (Fig. 1c). Obtained analogy between thermodynamic diagrams of the glassy state of matter and the bubble boiling of liquids is caused by the fluidity of the glass as liquid (“glass is liquid” (Tammann); undoubtedly, this is the best example of the phenomenon supporting well-known Frenkel’s kinetic theory of liquids). More over one can assume that the idea of the kinetic theory was “prompted” to Frenkel by Tammann’s glassy state, as probably form of Gibbs rule was “prompted” to him by Euler theorem about polyhedrons.

4. Conclusion

Modelling of fluids vertical convection in nature by means of our bubble-boiling method allowed us experimentally to investigate the thermodynamic parameters of solutions and their behavior during the whole process of heating. For more definition of the point of temperature discontinuity (T_{dc}) was introduced pseudo-entropy function ($\Sigma = Q/t^{0C}$), where temperature was measured in Celsius degrees. It is suggested to use pseudo-entropy parameter, Σ , in above mentioned cases. Then it was shown experimentally the likeness between the temperature-time (T, t)-diagrams of any matters water solutions and according crystal’s glassy state ones. We try also to find accordance between well-known Euler geometry and Gibbs thermodynamic equations. As a transition of non-isotropic state into other one is impossible, as a transition of isotropic state into non-isotropic one is impossible. In view of this property of crystals, I think that it is possible to find among of many-component systems the corresponding sample. Analysis shows that such object is the four-component system, which will give us to use Tammann’s thermodynamic tetrahedron for example. For making more precise of the moments of the liquids bubble-boiling micro- and macro-scale regimes appearances, respectively at $T = 40$ °C and $T = 80$ °C, we also constructed the graph $(d^2T/dt^2, T)$ in Fig. 4. Here we see as the points of contrary flexure at the value of temperature $T = 40$ °C and $T = 80$ °C (the curve $(dT/dt, T)$) are illustrated by means of the presence of two acute maximums on the curve $(d^2T/dt^2, T)$. As this was to be expected, the availability of these maximums near temperature 40 °C and 80 °C was not accident. It is interesting also to note that according maximums on the curve $(d^4T/dt^4, T)$ are narrower and lower than maximums of the curve $(d^2T/dt^2, T)$. We can conclude that an accurate measuring, for example, of the temperature, $T(t)$, is quite enough for exact definition of the micro- and macro-scale bubble-boiling regimes beginning moments without using, for example, of high-speed filming technique. Analogy between thermodynamic diagrams both of the glassy state of minerals and the bubble boiling of liquids is caused by the fluidity of the glass as liquid, that is, “glass is liquid” (Tammann); this is the best example of the phenomenon supporting Frenkel’s kinetic theory of liquids). Obtained results quite naturally are in the channel of Euler-Gibbs-Tammann-Frenkel classic works.

APPENDIX

The points of the second kind discontinuities (dc) on the experimental (T, t)-curves

Here it is represented the original universal experimental curve (T_{dc}, ρ_{dc}) obtained by us for water solutions of NaCl, $C_{12}H_{22}O_{11}$ and other matters (Fig. 5). The extremums of the curve $(d^2T/dt^2, T)$ on Fig. 4 accordance to these points (T_{dc}).

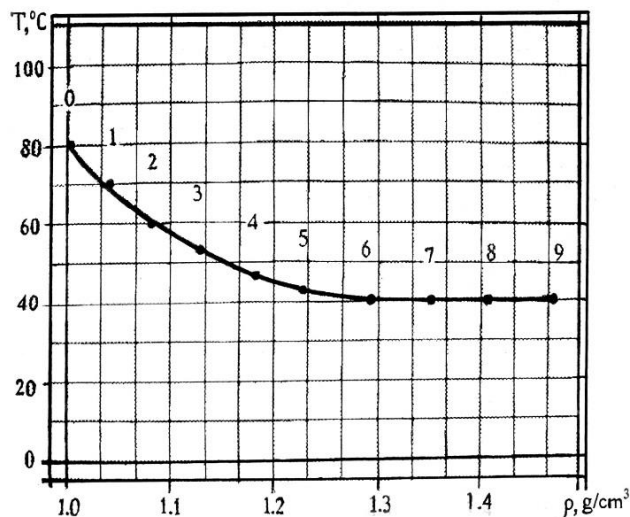


Fig. 5. The universal experimental curve of dependence of the temperature, T , of the second kind of discontinuity in time, to the concentration, ρ , of any matter water solution. (0) $\rho = 1.0 \text{ g/cm}^3$, (1) $\rho = 1.04 \text{ g/cm}^3$, (2) $\rho = 1.08 \text{ g/cm}^3$, (3) $\rho = 1.13 \text{ g/cm}^3$, (4) $\rho = 1.18 \text{ g/cm}^3$, (5) $\rho = 1.23 \text{ g/cm}^3$, (6) $\rho = 1.29 \text{ g/cm}^3$. (7) $\rho = 1.35 \text{ g/cm}^3$, (8) $\rho = 1.41 \text{ g/cm}^3$, (9) $\rho = 1.47 \text{ g/cm}^3$. The intensity of heating of solution $q = 47 \text{ J/s}$

Fig. 6 shows the original universal experimental curve (t_{dc}, ρ_{dc})-time-density dependence obtained by us both for the water solutions represented on Fig. 5 (●) and the natural waters of Georgia by means of the bubble-boiling points (x).

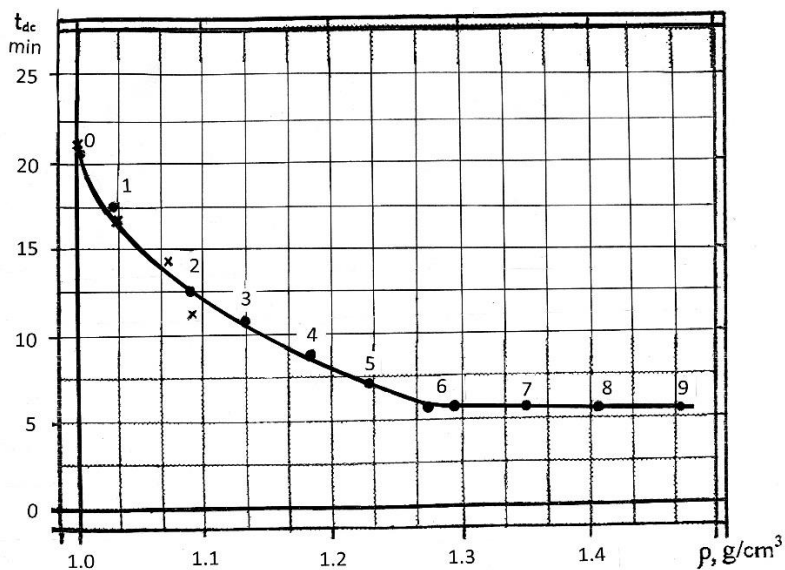


Fig. 6. The universal experimental curve of dependence of the temperature, T , of the second kind of discontinuity in time, to the concentration, ρ , of any matter water solution. The dark circle points (●) correspond to above mentioned artificial solutions with densities: (0) $\rho = 1.0 \text{ g/cm}^3$, (1) $\rho = 1.04 \text{ g/cm}^3$, (2) $\rho = 1.08 \text{ g/cm}^3$, (3) $\rho = 1.13 \text{ g/cm}^3$, (4) $\rho = 1.18 \text{ g/cm}^3$, (5) $\rho = 1.23 \text{ g/cm}^3$, (6) $\rho = 1.27$ and 1.29 g/cm^3 , (7) $\rho = 1.35 \text{ g/cm}^3$, (8) $\rho = 1.41 \text{ g/cm}^3$, (9) $\rho = 1.47 \text{ g/cm}^3$. The points (x) correspond to natural waters of Georgia with densities: (0) $\rho = 1.0 \text{ g/cm}^3$ (t. Tsalka), (1) $\rho = 1.02 \text{ g/cm}^3$ (Black Sea, near t. Anaklia), (2) $\rho = 1.07 \text{ g/cm}^3$ (sulfuric waters of Lisi Lake), (3) $\rho = 1.08 \text{ g/cm}^3$ (sulfuric waters of the old Tbilisi bathe house). (4) The intensity of heating of solution $q = 47 \text{ J/s}$.

The curves of Fig. 5 and Fig. 6 having similar behavior show high influence of the density of the solution on the beginning of its bubble-boiling regime during the process of heating. Therefore, between T_{dc} and t_{dc} exists linear low (result of joint action of the processes of temperature conductivity, thermals and vapour bubbles mixing convective motion). Therefore, for $q = \text{const.}$ we can write that $(dT/dp)_{dc} = \text{const.}$, $(dp/dt)_{dc} = \text{const.}$, and $(dS/dT)_{dc} = \text{const.}$

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თერმოდინამიკის გეომეტრიული ფორმალიზმი: სითხის ბუშტოვანი დუღილის და მინისებრი მდგომარეობის კონტექსტში

ა. გველესიანი

რეზიუმე

გეოსფეროში მიმდინარე ვერტიკალური კონვექციის მოდელირებისათვის ინსტიტუტის თერმობაროკამერის ბაზაზე შემუშავებულ იქნა სითხის ბუშტოვანი დუღილის მეთოდი (ზდმ), რომელმაც შესაძლებლობა მოგვცა შეგვესწავლა თერმოდინამიკური სისტემების (ბუნებრივი წყლების, წყლის ხელოვნური ხსნარების) პარამეტრების ყოფაცქევა გათბობის პროცესში თერმიკული-მიკრო და -მაკრო-ბუშტოვანი რეჟიმების გავლით ინტენსიურ დუღილამდე მიყვანისას. აგებულ და გაანალიზებულ იქნა (T, t) -, $(dT/dt, T)$ - და $(d^2 T/dt^2, T)$ - ექსპერიმენტული მრუდები, სადაც T სინჯის ტემპერატურაა, t -დრო (შემოთავაზებულ ადრე ფსევდო-ენტროპიის $\Sigma = Q/T$, სადაც გათბობის საწყის, თერმიკების რეჟიმში ტემპერატურა იზომებოდა ცელსიუსის გრადუსებში, $^{\circ}C$). მიკრო-და-მაკრო-ბუშტოვანი რეჟიმების ზუსტი მომენტების დადგენისათვის აგებულ იქნა $(dT/dt, T)$ - და $(d^2 T/dt^2, T)$ -მრუდები. ანალიზმა გვიჩვენა (T, t) -მრუდებზე (შეჯერებული ხსნარის $40^{\circ}C$ დასუფთა წყლის $80^{\circ}C$ წერტილებში) ადგილი ჰქონდა მეორე გვარის წყვეტას. ეს გარემოება თავს იჩენს გადახრის წერტილების სახით $(dT/dt, T)$ -მრუდებზე, ხოლო $(d^2 T/dt^2, T)$ - მრუდებზე – ორიმკვეთი ექსტრემუმის სახით (ექსტრემუმები აღინიშნა აგრეთვე $(d^4 T/dt^4, T)$ -მრუდზე). ამით საბოლოოდ დამტკიცდა შემოთავაზებული ბუშტოვანი დუღილის მეთოდის სიზუსტე და უპირატესობა შრომატევად რთულ ჩქაროსნულ კინოგადაღების ტექნიკის გამოყენებასთან შედარებით. ნაჩვენებია აგრეთვე წყლის ხსნარებისათვის აქ მიღებული (T, t) -მრუდების მსგავსება ტამმანის ნივთიერების მინისებრი მდგომარეობის დიაგრამებთან. ოილერის მრავალწახნაგების თეორემის და ჯიბბსის თერმოდინამიკური წესის შორის მსგავსების გამო (რაც ფორმით და შინაარსით ინტეგრირებულია ბუნებრივ თუ ხელოვნურ კრისტალში) გამოთქმულია მოსაზრება, რომ მრავალკომპონენტური სისტემისათვის ჯიბბს-ტამმანის მეთოდის მეშვეობით შესაძლებელია თერმოდინამიკური დიაგრამების გამოსახვა მრავალწახნაგების (ტეტრაედრის, კუბის, ოკტაედრის, ...) სახით. აღსანიშნავია, რომ ამ გზით თვით ტამმანმა ოთხკომპონენტური სისტემისათვის მიიღო ტეტრაედრი. და ბოლოს, უნდა ითქვას, რომ კრისტალების მინისებრი მდგომარეობის და სითხის ბუშტოვანი დუღილის დიაგრამებს შორის ზემოთ აღნიშნული მსგავსება არაა შემთხვევითი და აიხსნება ორივე სისტემის ძირითადი მახასიათებელი თვისებებით – დინებადობით (“მინა სითხეა” (ტამმანის). მაშასადამე, სითხის ბუშტოვანი დუღილის მეთოდის დიაგრამები ტამმანის დიაგრამებთან ერთობლიობაში ბრწყინვალე დეტანხმება ფრენკელის სითხის კინეტიკური თეორიის ძირითად კრიტერიუმს “მყარი სხეულის და სითხის სტრუქტურული მსგავსების” შესახებ. მეტიც, შეგვიძლია ვივარაუდოთ, რომ ფრენკელის სითხის კინეტიკური თეორიის იდეა “უკარნახა” ტამმანის შრომამ კრისტალის მინისებრი მდგომარეობის შესახებ, როგორც შესაძლოა ოილერის ფორმულამ მრავალწახნაგის შესახებ უნებლიედ ერთგვარი “ნატურის” როლი შეასრულა ჯიბბსის ფორმულისათვის ქიმიურად-ერთგვაროვანი ნივთიერების ფაზების წონასწორობის შესახებ.

Геометрический формализм термодинамики: в контексте пузырькового кипения жидкости и стеклообразного состояния вещества

А.И. Гвелесиани

Резюме

Моделирование вертикальной конвекции в естественных условиях оригинальным методом пузырькового кипения (ППМ) жидкости, разработанным автором, позволило экспериментально исследовать поведение термодинамической системы (образцов природных вод и искусственных водных растворов) в течение процесса их нагрева до интенсивного крупнопузырькового кипения. Для точного установления моментов наступления микро-и макро-масштабного режимов пузырькового кипения жидкости были построены и проанализированы экспериментальные кривые зависимостей: (T, t) – температура-время, $(dT/dt, T)$ – скорость нарастания температуры- температура, $(d^2T/dt^2, T)$ – ускорение нарастания температуры-температура. Построение двух последних кривых было обусловлено наличием разрывов непрерывности второго рода в (T, t) - кривых (без привлечения энтропии (S) и введённой нами “псевдоэнтропии” (Σ) , где температура бралась в $^{\circ}C$). Для точного установления моментов наступления микро- и макро-масштабного режимов пузырькового кипения жидкости были построены кривые зависимости скорости $(dT/dt, T)$ и ускорения $(d^2T/dt^2, T)$ нарастания температуры от температуры, T . В результате при $40^{\circ}C$ и $80^{\circ}C$ точки перегиба кривой $(dT/dt, T)$ проявились, как и следовало ожидать, в виде ярко выраженных максимумов на кривой $(d^2T/dt^2, T)$. Максимумы же кривых $(d^4T/dt^4, T)$ выражены значительно слабее). Таким образом, для точного установления моментов начала микро-и макро-масштабного режимов пузырькового кипения жидкости вполне достаточно внимательно фиксировать во времени рост температуры исследуемой жидкости, не прибегая к помощи трудоёмкой скоростной киносъёмки. Показано подобие между построенными диаграммами (T, t) для жидких растворов и соответствующими диаграммами стеклообразного состояния вещества Таммана. Делается попытка установить связь между геометрической формулой Эйлера и термодинамической формулой Гиббса. Тамманн пришёл к тетраэдру, рассматривая четырёхкомпонентную систему ($n = 4$). По-видимому, для многокомпонентных систем ($n = 4, 5, \dots$) методом, условно называя его методом Эйлера-Гиббса-Таммана можно будет прийти к кубу, октаэдру и пр. многогранникам, соответственно (тема следующей работы). Замеченная аналогия между термодинамическими диаграммами стеклообразного состояния кристаллов и пузырькового кипения жидкостей обусловлена тем, что стекло также текуче, как и жидкость, т.е. “стекло есть жидкость” (Тамманн) (пример, ярко подтверждающий кинетическую теорию жидкости Френкеля). Можно предполагать, что идея кинетической теории жидкости была “подсказана” Френкелю таммановским стеклообразным состоянием кристалла, как возможно эйлеровская формула о многогранниках послужила своего рода “натурой” для термодинамической формулы Гиббса о равновесном состоянии фаз химически-однородного вещества.