

Number-Theoretic Internal Energy for a Gas Mixture

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Abstract. For a gas mixture, the new concept of number-theoretic internal energy is introduced. This energy does not depend on the masses of the miscible gases.

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*To the memory of Evgenii Grigor'evich Maksimov,
a great physicist and a great human being.*

1. INTRODUCTION

The talented, straight-out, go-ahead physicist, a great expert in high-temperature superconductivity, Corresponding Member of the Division of Physics and Astronomy of the Russian Academy of Sciences, Evgenii Grigor'evich Maksimov, had left us. He was not only direct pupil of Ginzburg, he inherited the style of Ginzburg's school, and he was an even more abrupt, more "out-and-out" physicist than Ginzburg himself.

Since the author is an "out-and-out" mathematician himself, our scientific collisions and controversies with Zhenya reflect the difference between the mathematical and physical approaches in science as well as possible.

For me, for a mathematician, Zhenya's remarks, as well as the remarks of Ginzburg, were extraordinarily useful. I was always sincerely delighted with both of them.

I would like to save the unexpected and ingenious answers for the history of the collisions of these two branches of science. (I italicize his remarks below).

We were friends, but I had no faith in physics and he had no faith in mathematics. Frenkel', a remarkable physicist, wrote: "We become readily used to sameness and permanency, and cease of making note of it. The usual seems to be natural and comprehensible, the unusual seems to be unnatural and incomprehensible . . . Really and truly, we cannot understand, we can only get used to." (V. Ya. Frenkel'. Yakov Il'ich Frenkel' ("Nauka," Moscow–Leningrad, 1966).) I had no faith in this "usual" if it has no rigorous proof.

As an example of different logical approaches to science, I can present an episode concerning the negative referee's report concerning a paper by Arnold who had sent this paper to ZhETF (JETP). He described this episode in his memoirs.

Similar things happened sometimes to me. Once upon a time, when I was young, after being a guest, I walked together with L.F., a physicist who worked in the Landau institute. We had a controversy concerning the notion of semiclassical asymptotics.

I carried out the proof on the snow rather than "on sand" (it was winter) and claimed that the tunnel asymptotics leading to splitting of vacuum vectors (nowadays, these are referred to as instantons) is a semiclassical asymptotics.¹This was our only meeting. However, when I was already a Member of the Academy and an acknowledged expert in semiclassics, my interlocutor gave a drastic negative referee's report about one of my papers and wrote that I cannot understand at all what is the semiclassical asymptotics.

I remember our controversies with Zhenya Maksimov nearly five years ago at my country house. I said: "I wonder how it may be that, in Landau's book concerning quantum statistics, there are two definitions of the Bose statistics. One of them uses combinatorics, and the other the symmetry of the eigenfunctions of the N -particle Schrödinger equation, and no formulas are presented to relate these definitions to each other."

"Well, the first definition is archaic. Everybody now uses the other one."

¹I could not convince the physicists. They were convinced by the new notion, namely, Euclidean field theory. They became familiar with this notion very soon.

“What will happen if the students will ask about their relationship? ”

“*They won’t ask,*” answered Zhenya with confidence.

The superfluidity and superconductivity are closed problems. In 2005, using a purely mathematical approach, I obtained a paradoxical fact concerning the superfluidity of water in a nanotube. I told Maksimov about this. He said: “*You won’t convince me by your lemmas.*” I will remember this sentence as long as I live; I then understood that the explanation for physicists must be of another nature.

I invented an explanation which was more or less perceived by physicists: the rays reflected from the wall of a capillary can be treated as the collision of two rays one of which moves forward in time and the other moves backward in time, as an electron and positron (“A positron is an electron moving backwards in time” (Feynman)).² The collision of the rays leads to the creation of a photon, which is absorbed by the wall, and the motion is retarded. For this reason, the radius of the tube should be so small that no rays of this kind could happen. Then the absorption and the retardation are absent, and superfluidity occurs. This explanation led to the appropriate associations of the physicists.

From the point of view of philosophy, this explanation is a more complicated construction than the introduction by the author of the operators of creation and annihilation of pairs in the ultra-second quantization and the derivation of the corresponding equation from the asymptotic limits.

One of the greatest physicists of the present time warned me: “If you will continue claiming that there is a Bose condensate in the two-dimensional case, I shall vote against your nomination” (for the award of a prize, *VM*). This occurred although the existence theorem for the Bose condensate in the two-dimensional case had already been proved by me. Next time, the requirement to renounce one of my papers was demanded from me as a necessary condition of giving me by a rather large grant by Russian Federation.

A human intimidated by theoretical physicists has to get rid, for instance, of an old family diamond, because, by the theory of Maxwell transition, the diamond is in a metastable state, and, in the course of time, it will certainly be transformed to graphite.

In 2008, the Livermore laboratory (Lawrence Livermore National Laboratory, Livermore, USA) sent me a series of papers describing experiments confirming the superfluidity in nanotubes. From the beginning, Maksimov did not believe these data. However, our joint detailed consideration of these works removed all his doubts. In this consideration, he taught me to carefully consider experimental data.

Last year, I sent a paper to the journal “Physics-Uspekhi” [“Uspekhi Fizicheskikh Nauk”] for the issue dedicated to V. L. Ginzburg. I asked the new Editor-in-Chief of the journal to send the paper for referee’s report to the “fiercest” referee, i.e., to Maksimov. Zhenya studied the work, understood everything perfectly, and forced me to rewrite the paper completely. In this process, he kept in the paper pure real world arguments and analogies rather than mathematical considerations.

Ernst Mach, the great physicist and philosopher, wrote in his popular lectures: “It has surely often struck you as strange that the sciences are divided into two great groups; that the so-called humanistic sciences, belonging to the so-called “higher education,” are placed in almost a hostile attitude to the natural sciences... I must confess I do not overmuch believe in this partition of the sciences. I believe that this view will appear as childlike and ingenuous to a matured age.” (Ernst Mach, *Popular Scientific Lectures*, English transl. by Thomas J. McCormack (The Open Court Pub. Co., London, 1898), p. 86). I wondered why Zhenya did not order to delete from a physical paper (and even approved) a real world analogy with the Fermi statistics where I cited the rollicking picaresque novel “The Twelve Chairs” by Il’f and Petrov. In the novel, a situation is described in which inhabitants are “in the grip of an acute food and commodity shortage. Representatives from the co-operatives and state-owned trading organizations proposed that until the arrival of food

²“In this solution, the “negative energy states” appear in a form which may be pictured (as by Stueckelberg) in space-time as waves traveling away from the external potential backwards in time. Experimentally, such a wave corresponds to a positron approaching the potential and annihilating the electron. A particle moving forward in time (electron) in a potential may be scattered forward in time (ordinary scattering) or backward (pair annihilation). When moving backward (positron), it may be scattered backward in time (positron scattering) or forward (pair production). For such a particle, the amplitude for transition from the initial to the final state is analyzed to any order in the potential by considering that it undergoes a sequence of such scatterings.” R. P. Feynman, “The Theory of Positrons,” *Phys. Rev.* **76**, 749–759 (1949).

supplies, already on their way, the sale of comestibles should be restricted to a pound of sugar and five pounds of flour a head.” To get a maximal possible amount of sugar and flour by correctly using a queue, at “the head of the sugar queue stood Alchen. Behind him was his wife, Sashchen, Pasha Emilevich, four Yakovleviches and all fifteen old-women pensioners in their woollen dresses.” (I. Ilf and E. Pertov, *The Twelve Chairs*, English transl. by John Richardson (Sphere Books, 1971 (1928)). It is clear that, from the point of view of the sugar and flour purchased by the bunch of rogues, it does not matter in what order the members of the group are placed, and they can be transposed without any loss. At the same time, there is no reason to occupy the same place by two persons. In this sense, the “Pauli exclusion principle” is fulfilled. Thus, the “exclusion” is established by us by ourselves, because it is advisable.

Zhenya said: “Yes, the grannies are indistinguishable from the point of view of buying goods, and it is senseless for two persons to stand at the same point of the queue indeed.”

I have cited some of Maksimov’s sentences in detail to keep him alive not only in my own memory, and so that his unforgettable fighting character would be reflected in these lines, at least partially.

2. CORRECTION TO THE BOSE–EINSTEIN DISTRIBUTION AND FRACTIONAL DIMENSION

I added Maksimov’s careful treatment of experimental data to my armoury when my construction of the spinodal point for metastable negative pressure computed for fractional dimensions less than two did not coincide with the experimental curve for water (this curve is presented in many sources). In these experiments, no jump of pressure when passing the zero pressure was discovered, although this jump is quite obvious. Indeed, an analog of the Young modulus for the compression and tension for water is different. Namely, water is almost incompressible under compression, whereas microvoids of cavitation type occur under tension. This convinced V. S. Vorob’ev, a well-known expert in modern thermodynamics. He believed that my correction to the Bose–Einstein distribution is valid and sent me his informal proof, which seems to me to be more convincing than Einstein’s proof (the latter selects a single point of the discrete spectrum and passes to the continuous limit with respect to the other points of this spectrum).

Let me present this “proof” by Vorob’ev (the derivation of the formula for the Bose gas).

We have

$$\Omega_k = -T \log \sum_{n=1}^N \left(\exp \frac{\mu - \varepsilon_k}{T} \right)^n, \quad n = 0, 1, 2, \dots, N, \tag{1}$$

where N stands for the number of particles. Summing the finite geometric progression, we obtain

$$\Omega_k = -T \log \left(\frac{1 - \exp \frac{\mu - \varepsilon_k}{T} N}{1 - \exp \frac{\mu - \varepsilon_k}{T}} \right). \tag{2}$$

Further,

$$\Omega_k = -T \sum_k \log \left(\frac{1 - \exp \frac{\mu - \varepsilon_k}{T} N}{1 - \exp \frac{\mu - \varepsilon_k}{T}} \right). \tag{3}$$

Passing in the standard way from the summation over k to integration with respect to the energy, we see that

$$\Omega = -\frac{gV}{\Lambda^3} T \frac{2}{\sqrt{\pi}} \int_0^\infty t^{1/2} dt \log \left(\frac{1 - \exp(\mu/T - t)N}{1 - \exp(\mu/T - t)} \right), \tag{4}$$

where

$$\Lambda = \frac{h}{(2\pi mT)^{3/2}}, \quad t = \varepsilon/T.$$

Integrating (4) by parts, we obtain

$$\Omega = \frac{gV}{\Lambda^3} T \frac{2}{\sqrt{\pi}} \frac{2}{3} \int_0^\infty t^{3/2} dt \left(\frac{1}{\exp(t - \mu/T) - 1} - \frac{N}{\exp(t - \mu/T)N - 1} \right). \tag{5}$$

Formula (5) written out for a fractional dimension becomes

$$\Omega = \frac{gV_\gamma}{\Lambda^{2(1+\gamma)}} T \frac{1}{\Gamma(2+\gamma)} \int_0^\infty t^{1+\gamma} dt \left(\frac{1}{\exp(t - \mu/T) - 1} - \frac{N}{\exp(t - \mu/T)N - 1} \right), \quad (6)$$

where

$$V_\gamma = L^{\gamma(1+\gamma)}$$

and L stands for the typical size of the system.

The dimension varies from $D = 2$ to $D = 3$. The quantity γ characterizing the fractional dimension is given by

$$D = 2(1 + \gamma).$$

We have the formula

$$N = -\partial\Omega/\partial\mu$$

for the number of particles, where

$$\Omega = \frac{gV_\gamma}{\Lambda^{2(1+\gamma)}} \frac{1}{\Gamma(1+\gamma)} \int_0^\infty t^\gamma dt \left(\frac{1}{\exp(t - \mu/T) - 1} - \frac{N}{\exp(t - \mu/T)N - 1} \right). \quad (7)$$

The quantity γ varies from zero (for $D = 2$) to 0.5 (for $D = 3$).

It is convenient to represent formula (6) by introducing the polylogarithms

$$\text{Li}_s(x) = \frac{1}{\Gamma(s)} \int_0^\infty \frac{t^{s-1}}{(e^t/x) - 1} dt. \quad (8)$$

Then we obtain

$$\Omega = \frac{gV_\gamma}{\Lambda^{2(1+\gamma)}} T \left(\text{Li}_{2+\gamma}(z) - \frac{1}{N^{\gamma+1}} \text{Li}_{2+\gamma}(z^N) \right), \quad (9)$$

where

$$z = e^{\mu/T}$$

stands for the action.

This gives

$$N = \frac{gV_\gamma}{\Lambda^{2(1+\gamma)}} \left(\text{Li}_{1+\gamma}(z) - \frac{1}{N^\gamma} \text{Li}_{1+\gamma}(z^N) \right). \quad (10)$$

We have $\gamma \rightarrow 0$ in the two-dimensional case, and, as $\mu \rightarrow 0$ ($z \rightarrow 1$), the second term in (9) and (10) becomes essential.

In the above derivation, the passage from sums to integrals for sufficiently large N is not rigorous. There is a lack of estimates, according to the Euler–Maclaurin summation formulas, that “do not spoil” the final result, and also a lack of estimates of the type presented in [1]. However, in any case, this derivation is more rigorous than the so-called “proof” of the absence of the Bose condensate in the two-dimensional case, which can be found in all handbooks, where only one point of the discrete spectrum is singled out (the minimal energies), whereas the passage to the integral is made with respect to all other points.

Certainly, a rigorous mathematical construction is more complicated than associations, “rules of the game,” and analogies that correspond to physical constructions. In his own approach, the author used rigorous constructions from probabilistic number theory and applied these constructions to problems in science and economics.

The author himself was not able to compare his mathematical results with experimental data, while this is the only way an influence physicists, in the aggregate, because physicists are accustomed to simpler notions and phenomenological constructions. Therefore, to explain his theory, the author is forced to use terminology (from diverse areas) that are customary to physicists, so that, by using associations and at least approximately, they could be able to understand the constructions used by the author.

Among these notions that have nothing in common with the mathematical constructions, we can mention

- (1) fractal dimension;
- (2) Bose gas and the Bose–Einstein distribution;
- (3) internal energy;
- (4) the Ω -potential, and some other notions.

As far as the notion that was untitled “fractal dimension” by the author is concerned, it means only the density of the spectrum of a molecule in question and is related to the interaction between particles only with respect to the fact that the interaction itself depends on this density. This means that the spectrum and its density are primary. The very density leads to the new ideal gas of particles that do not interact with one another.

However, as can be seen by the example given by the scattering of particles interacting according to the Lennard–Jones potential [2], the value of Z_{cr} can be determined with a rather high accuracy. However, the value of Z_{cr} is only an approximate one for the new ideal gas. Taking the Zeno line into account leads to a nonideal correction for $Z_{\text{cr}}^{\text{id}}$.

3. NT-INTERNAL ENERGY

Let us now dwell on the Bose gas. For the case in which all particles have the same mass, we have indeed a coincidence with the Bose gas of fractional dimension (with respect to the momenta!). However, this construction contradicts the so-called “principle of identical particles” in quantum mechanics. Physicists explained this contradiction from the point of view of the passage from quantum mechanics to classical mechanics, by dividing the partition function by $N!$. This is a serious mathematical mistake. However, this satisfied the physicists, as well as philosophers of Kedrov’s school who favor the “union of opposites”, namely, on one hand, the particles are distinguishable (due to Boltzmann’s statistics), and, on the other hand, these particles are indistinguishable, because we divide by $N!$.

A special role in distinguishability–indistinguishability is played by the masses of the particles. If the masses are equal (or almost equal, like in the case of isotopes), then the particles are indistinguishable. In this sense, the Bose–Einstein statistics coincides with number theory.

Moreover, there is a remarkable van der Waals law of corresponding states in which, practically, only one dimensionless quantity is preserved that characterizes the state of the system, namely, the compressibility factor Z . In this case, the internal energy of the Bose gas coincides with the number \mathcal{E} partitioned into a sum of n summands. There is no such coincidence for gas mixtures.

It is worth recalling here experiments of Jean Perrin and Theodor Svedberg in 1908 (Nobel Prize in 1926) carried out by the ultramicroscope of Richard Adolf Zsigmondy (Nobel Prize in 1925). Perrin and Svedberg counted the number of aerosols (particles) of different mass in a given volume. In this case, one can also introduce the notion of internal NT-energy (Number Theory energy) which coincides with the number \mathcal{E} partitioned into a sum of N summands. This internal NT-energy coincides with the internal energy of the mixture of Bose gases if we set all masses of the particles to be equal to one. Nevertheless, in the theory of mixtures, it plays an extremely important role both for the definition of a new ideal gas of the mixture and in the computation of the Zeno line (the “ideal curve” of the mixture).

A more general way to define the number of particles of different masses can be realized by using scintillation.³

The notion of internal energy for Brownian particles (aerosols) in the Einstein–Smoluchowski theory does not depend either on the masses of the particles: as is well known, this gives $kT/2$ for every degree of freedom, i.e., this is equal to $3kT$ in the three-dimensional case and does not depend on the value of the mass.

Remark 1. The mass of the particles is taken into account when evaluating the mean.

Therefore, the NT-internal energy agrees with the above evaluation of the mean energy of aerosols. It can also be referred to as the aerosol internal energy.

³The scintillation (from the Latin original verb “scintillātiō,” something between “sparkle” and “flicker”) is a short-term (10^{-4} – 10^{-9} s) light flash (luminescence flash) occurring in scintillators under the action of ionizing radiations.

If the values \mathcal{E}_1 and \mathcal{E}_2 partitioned into sums of N_1 and N_2 summands, respectively, correspond to fractional dimensions γ_1 and γ_2 , respectively, and if the values of the pairs $\mathcal{E}_1 N_1$ and $\mathcal{E}_2 N_2$ are at the “border-line of degeneration,” i.e., adding an extra number to N_1 and to N_2 leads to “settling-out into a Bose condensate,” then for the sum $\mathcal{E}_1 + \mathcal{E}_2$ and for the number $N_1 + N_2$, adding an extra number to $N_1 + N_2$ also leads to “settling-out into a Bose condensate.”

Let ρ_1^{cr} and ρ_2^{cr} be the critical densities (in g/cm³) and m_1 and m_2 be the masses of molecules of the corresponding gases. The values N_1 and N_2 are proportional to the molar concentrations,

$$\frac{N_1}{N_1 + N_2} = \alpha, \quad (11)$$

$$\frac{N_2}{N_1 + N_2} = \beta, \quad (12)$$

$$N = N_1 + N_2, \quad \alpha + \beta = 1. \quad (13)$$

In this case, for the full NT-internal energy we obtain the relation

$$(\gamma^{\text{cr}} + 1)Z^{\text{cr}}T^{\text{cr}} = \alpha(\gamma_1^{\text{cr}} + 1)Z_1^{\text{cr}}T_1^{\text{cr}} + \beta(\gamma_2^{\text{cr}} + 1)Z_2^{\text{cr}}T_2^{\text{cr}}, \quad (14)$$

and it follows from the additive property of the entropy for $\mu = 0$ that

$$Z^{\text{cr}}(\gamma^{\text{cr}} + 2) = \alpha(\gamma_1^{\text{cr}} + 2)Z_1^{\text{cr}} + \beta(\gamma_2^{\text{cr}} + 2)Z_2^{\text{cr}}. \quad (15)$$

These two relations enable us to define $\gamma_{\text{sum}}^{\text{cr}}$ and $T_{\text{sum}}^{\text{cr}}$ for the ideal gas of the mixture. For the critical pressure, we have

$$P^{\text{cr}} = T^{\text{cr}} Z^{\text{cr}} N^{\text{cr}} R,$$

where R stands for the universal gas constant.

However, we are interested only in the values μ_1 and μ_2 that correspond to the Zeno line of each of the gases (see the formula (49) in the paper [14]).

The equations (11)–(13) imply the following equation for the sum of entropies, where $\kappa = \mu/T$:

$$(\gamma + 2)Z_{\gamma+2}(e^\kappa) - \kappa = \alpha\{(\gamma_1 + 2)Z_{\gamma_1+2}(e^{\kappa_1}) - \kappa_1\} + \beta\{(\gamma_2 + 2)Z_{\gamma_2+2}(e^{\kappa_2}) - \kappa_2\}; \quad (16)$$

the value $Z_{\gamma+2}$ is equal here to the ratio $\text{Li}_{\gamma+2}(e^\kappa)/\text{Li}_{\gamma+1}(e^\kappa)$.

Recall that the values κ_1 and κ_2 are chosen according to the Zeno line of the first and second gas, respectively. Hence, for the given values γ , γ_1 , and γ_2 obtained from (15), we obtain the value κ_{sum} , which defines the function $\varphi_\gamma(V)$ by relation (49) in the paper [14].

Remark 2. Note that it is not rigorously proved in the cycle of papers of the author that to any “pure” gas there corresponds a Zeno line. As is known, for example, the ideal curve is substantially curved for water under low densities. He have rigorously obtained the Zeno line only for the Lennard–Jones interaction potential. The same proof can be carried out for other interaction potentials. Therefore, one can agree that, for pure gases interacting according to the same potential, the Zeno line is approximately a line segment (and this segment is far from being straight in problem (25)–(30) of the paper [15]).

When passing to the liquid, the percentage of the gases is changed. Here one can apply the scheme of the “law of mass action,” however, to number theory, to the NT-internal energies. For a small correlation sphere in the fluid, one must consider all possible combinations of molecules and all stoichiometric coefficients corresponding to them. Under the assumption that the NT-internal energies are preserved, we obtain the same relations for the chemical potentials as those obtained in the law of mass action. After this, we obtain a system of equations with the corresponding family of unknowns.

Solving this system, we obtain the mean value of the concentrations of two pure gases in a liquid.

4. SPINODAL POINTS FOR THE LIQUID CASE

Since we consider diverse gases of different fractional dimensions, it is reasonable, when considering the van der Waals normalizations

$$P_{\text{red}} = \frac{P}{P_{\text{cr}}}, \quad T_{\text{red}} = \frac{T}{T_{\text{cr}}}$$

to keep only the first of these normalizations in the law of corresponding states,

$$P_{\text{red}}^\gamma = \frac{P^\gamma}{P_{\text{cr}}^\gamma},$$

and this normalization forms a new value T_{cr} , which is in essence the ratio $T_{\text{cr}}/P_{\text{cr}}$ up to a constant which makes this ratio dimensionless.

However, if we compare diverse gases and study their homogeneous mixtures, then it is most natural to consider the normalization on T_{cr} for hydrogen, neon, and helium 4, because, for these elements, the value of Z_{cr} is maximal among all gases (we do not consider the normalization with respect to mercury, because no homogeneous mixtures for mercury are known).

In this case, for the classical gas of dimension γ , the critical temperature is given by a number less than one:

$$T_{\text{cr}}^{(\gamma)} = \left(\frac{\zeta(\gamma_0 + 2)}{\zeta(\gamma + 2)} \right)^{1/(\gamma+2)} \tag{17}$$

where $Z = 0.30$ for neon. After this, we find the point of the spinodal of the liquid phase corresponding to this critical temperature and, finally, normalize with respect to the point thus obtained.

We have assumed in [2] that all solutions of the Diophantine equations (7), (8) are equiprobable. As we have shown by the example of partitioning \mathcal{E} banknotes among N spectators [2], if $N > N_{\text{cr}}$, then $N - N_{\text{cr}}$ spectators will have no banknotes at all. Here it was certainly assumed that

$$N/N_{\text{cr}} \geq 1 + \delta,$$

where $\delta > 0$ is an arbitrarily fixed number, and that the relations

$$N \rightarrow \infty, \quad \mathcal{E} \rightarrow \infty, \quad \text{and} \quad \mathcal{E} \gg N$$

are also satisfied. As we have already written several times, this fact corresponds to the Bose condensate in physics, whereas it can determine, for example, the number of the unemployed in economics.

An alternative to this phenomenon in number theory is the union into pairs for $N = 2N_{\text{cr}}$ and, as N increases, into clusters. As was already mentioned above, the union leads to reducing the dimension, which corresponds to reducing the number of degrees of freedom for the members of the union.

The following question arises: How to unite optimally, i.e., how to reduce the dimension in the best possible way? The reduction of the dimension (related to the “number of degrees of freedom”) happens in economics both at the expense of unions and at the expense of restricting the “market freedom” by laws. How to choose the best possible way?

In the example with Korov’ev, which was used in the author’s works many times,⁴ it was mentioned that, for the spectators, it is sufficient to combine themselves into groups with ten persons each, and then every group will obtain at least one banknote with a great probability, the members of the group will divide the money, and nobody will die of hunger. This procedure will lead to a significant drop of entropy, because, in every group, the distribution of money obtained in this way is carried out in accordance with some law; for example, in equal parts.

⁴According to Bulgakov’s novel *Master and Margarita* Korov’ev’s trick consisted scattering 1,000,000 banknotes in the variety theater occupied by 10,000 spectators.

However, there is the possibility of uniting totally and to “honestly” divide the entire million of banknotes scattered by Korov’ev. In this version, the entropy drops to zero.

In each of the cases, the main task is solved, namely, all spectators remain alive, which means in thermodynamics that the number of particles is preserved. However, the problem is to preserve the number of spectators (or particles) in such a way that the number of persons in any union is the minimal possible. This means that one must obtain the maximal possible dimension under the assumption that the number of particles is preserved.

We shall refer to such a passage to the maximal dimension as the passage to the liquid state. Whereas, for the gaseous branch of the isotherm, we took the dimension $\gamma = \gamma_0$ and did not change this value for $\gamma > \gamma_0$, it should be noted that, for the liquid branch, the value γ is reduced provided that the temperature is reduced, and hence the value Z_{cr}^γ is also reduced in this case.

Obviously, as the temperature is reduced, the number of particles in the union, i.e., the number of molecules in clusters, increases. To obtain this increase, we must *increase* the initial temperature (for $\gamma = \gamma_0$) so that the entropy, for the initial number of solutions of the Diophantine equations will increase. Then the number of molecules in the union (the cluster) becomes greater. This means that we must increase the value T_{cr} in the initial formula for the entropy. Thus, if the real temperature of the liquid phase is decreased, we must increase the relative temperature T_{cr} in the original formula for the entropy.

This means that the relative temperature increases at Z^{γ_0} , and the original entropy becomes

$$S = \left(\frac{T}{T_{liq}} \right)^{\gamma+1} (\text{Li}_{\gamma+2}(e^{-\xi})(\gamma+2) + \xi \text{Li}_{\gamma+1}(e^{-\xi})), \quad (18)$$

where $\xi = -\mu/T$, μ stands for the chemical potential, Li for the polylogarithm, and γ for the dimension, see [3].

Remark 3. The polylogarithm $\text{Li}_{\gamma+2}(e^{-\xi})$ is of the form

$$\text{Li}_{\gamma+2}(e^{-\xi}) = \sum \frac{e^{-k\xi}}{k^{\gamma+2}} = \sum \frac{e^{-k\xi - \gamma \log k}}{k^2}.$$

Its derivative with respect to γ is equal to

$$\frac{\partial}{\partial \gamma} \text{Li}_{\gamma+2}(e^{-\xi}) = - \sum \frac{\log k e^{-k\xi - \gamma \log k}}{k^2}.$$

For $\mu = 0$, we obtain

$$S|_{\mu=0} = \left(\frac{T}{T_{liq}} \right)^{\gamma+1} \zeta(\gamma+2)(\gamma+2), \quad (19)$$

where ζ stands for the Riemann zeta function.

This gives a simple condition for the maximization of γ ,

$$\left. \frac{dS}{d\gamma} \right|_{\xi=0} = 0, \quad \log \left(\frac{T}{T_{liq}} \right) \zeta(\gamma+2)(\gamma+2) + \zeta'_\gamma(\gamma+2)(\gamma+2) + \zeta(\gamma+2) = 0, \quad (20)$$

$$-\frac{d \log \zeta(\gamma+2)}{d\gamma} = \log \left(\frac{1}{T_{liq}} \right) + \frac{1}{\gamma+2}. \quad (21)$$

In this case, the solution of (20) gives $\gamma = 0.14$, and hence

$$Z_{\gamma_1(\gamma_0)} = 0.24.$$

Since $N = \text{const}$, it follows that, on the isotherm, we have

$$P_{\gamma_1} = \text{const} \cdot Z_{\gamma_1}.$$

The points $Z_{\gamma_1}, P_{\gamma_1}$ are the spinodal points for the liquid phase, i.e., the points of termination for the metastable state of the liquid phase.⁵

Remark 4. The method of gradient descent with respect to entropy describes an unstable part, and its trajectory is not observed in experiments. However, for the graphs to have no discontinuities for the gaseous and liquid phases, it is more customary to solve the equation of gradient descent from γ_0 to $\gamma_1(\gamma_0)$, from the point $\gamma = \gamma_0, \xi = 0$ up to the point $\gamma_1 = 0.18$.

For hydrogen, we must set

$$T_{\text{red}} = T/T_{\text{cr}},$$

i.e., $T_{\text{red}} = 1$ for $T = T_{\text{cr}}$. If $T < T_{\text{cr}}$, then

$$T_{\text{red}}^{\text{liq}} = T/T_{\text{cr}}.$$

Since at any point of the liquid, for $\gamma < \gamma_1$, the temperature is less than T_{cr} , and still, to any point, there corresponds its own related value of Z_{cr}^γ , it is convenient to normalize every value of Z_{cr}^γ with respect to the value of T_{liq}^γ corresponding to this value of Z_{cr}^γ , which means that

$$T_{\text{red}} = \frac{1}{T_{\text{cr}}},$$

i.e., the value $T_{\text{cr}}^{\gamma_0}$ (and hence the entropy S as well) is increased and becomes a new value T_{cr} equal to $1/T_{\text{red}}$ for the liquid. Moreover,

$$S_{\gamma_0} = T_{\text{cr}}^{\gamma+1} (\text{Li}_{\gamma_0+2}(e^{-\xi})(\gamma_0 + 2) + \xi \text{Li}_{\gamma_0+1}(e^{-\xi})). \tag{22}$$

Thus, we set $T = 1/T_{\text{liq}}$ in the formulas 15-17.

A gas is said to be *quasi-ideal* if

$$\varphi'_\gamma(V) = \text{const}$$

(see [3]). In this case, the Zeno line appears the definition of the spinodal points of the liquid phase; however, the liquid remains incompressible. Only the consideration of the function $\varphi_\gamma(V)$ enables one to bend the straight lines and take into account the fact that the liquid is compressible. Nevertheless, for $T_{\text{liq}} \ll 1$, i.e., for sufficiently small (and still positive) values γ , the influence of the value $\varphi_\gamma(V)$ is already inessential. Therefore, a quasi-ideal gas, and especially a mixture of quasi-ideal gases, gives a sufficiently good approximation for the spinodals of the liquid phase.

The geometrical locus of the points of quasi-ideal spinodals⁶ is given by the formula

$$P = T\rho_B \left(1 - \frac{T}{T_B}\right) Z_{\text{cr}}^\gamma, \tag{23}$$

where ρ_B and T_B stand for the Boyle density and Boyle temperature, respectively.

Here we have

$$Z_{\text{cr}}^{\gamma(T_{\text{liq}})} = \frac{\zeta(2 + \gamma(T_{\text{liq}}))}{\zeta(1 + \gamma(T_{\text{liq}}))}, \quad T = T_{\text{liq}}. \tag{24}$$

Recall that $\gamma(T_{\text{liq}})$ is evaluated by using the algebraic relation (21).

Every point on the quasi-ideal spinodal is joined to the point, corresponding to the given value of (T_{liq}) , located on the Zeno line placed to the left of the critical line for $(T_{\text{liq}}) = 1$.

For $\gamma(T) < 0$, we use the correction, to the Bose–Einstein distribution, which was introduced by the author (see Section 2).

⁵A metastable state of the liquid phase can exist a billion of years, even under negative pressure (see the above example concerning the diamond).

⁶In other words, of the points of termination of the metastable state of the liquid phase.

Let us find the constants b and κ from the following relations:

$$\int_0^\infty \xi \left\{ \frac{1}{e^{b(\xi+\kappa)} - 1} - \frac{N}{e^{bk(\xi+\kappa-1)}} \right\} \xi^\gamma d\xi = \mathcal{E}, \quad (25)$$

$$\int_0^\infty \left\{ \frac{1}{e^{b(\xi+\kappa)} - 1} - \frac{N}{e^{bk(\xi+\kappa-1)}} \right\} \xi^\gamma d\xi = N, \quad (26)$$

where

$$\kappa = -\mu, \quad b = 1/T.$$

Write $n = \mathcal{E}$. For $\kappa = 0$, we have

$$n = \int \frac{\xi d\xi^\alpha}{e^{b\xi} - 1} = \frac{1}{b^{1+\alpha}} \int_0^\infty \frac{\eta d\eta^\alpha}{e^\eta - 1}, \quad (27)$$

where $\alpha = \gamma + 1$. This implies that

$$b = \frac{1}{n^{1/(1+\alpha)}} \left(\int_0^\infty \frac{\xi d\xi^\alpha}{e^\xi - 1} \right)^{1/(1+\alpha)}. \quad (28)$$

Write $N_{\text{cr}} = k_0$. We obtain

$$\begin{aligned} k_0 &= \int_0^\infty \left\{ \frac{1}{e^{b\xi} - 1} - \frac{k_0}{e^{k_0 b \eta} - 1} \right\} d\xi^\alpha \\ &= \frac{1}{b^\alpha} \int_0^\infty \left(\frac{1}{e^\xi - 1} - \frac{1}{\xi} \right) d\xi^\alpha + \frac{1}{b^\alpha} \int_0^\infty \left(\frac{1}{\xi} - \frac{1}{\xi(1 + (k_0/2)\xi)} \right) d\xi^\alpha \\ &\quad - \frac{k_0^{1-\alpha}}{b^\alpha} \int_0^\infty \left\{ \frac{k_0^\alpha}{e^{k_0 \xi} - 1} - \frac{k_0^\alpha}{k_0 \xi(1 + (k_0/2)\xi)} \right\} d\xi^\alpha. \end{aligned} \quad (29)$$

Write

$$c = \int_0^\infty \left(\frac{1}{\xi} - \frac{1}{e^\xi - 1} \right) \xi^\gamma d\xi.$$

After the change $k_0 \xi = \eta$, we obtain

$$\begin{aligned} &\frac{k_0^{1-\alpha}}{b^\alpha} \int_0^\infty \left\{ \frac{k_0^\alpha}{e^\eta - 1} - \frac{k_0^\alpha}{\eta(1 + \eta/2)} \right\} d\xi^\alpha \\ &= \frac{k_0^{1-\alpha}}{b^\alpha} \int_0^\infty \left\{ \frac{1}{e^\eta - 1} - \frac{1}{\eta(1 + \eta/2)} \right\} d\eta^\alpha \\ &= \frac{k_0^{1-\alpha}}{b^\alpha} \left\{ \int_0^\infty \left(\frac{1}{e^\eta - 1} - \frac{1}{\eta} \right) + \int_0^\infty \frac{d\eta^\alpha}{2(1 + \frac{\eta}{2})} \right\} = -c \frac{k_0^{1-\alpha}}{b^\alpha} + c_1 \frac{k_0^{1-\alpha}}{b^\alpha}. \end{aligned} \quad (30)$$

Since

$$\frac{1}{\eta(1 + \eta/2)} = \frac{1}{\eta} - \frac{1}{2(1 + \eta/2)},$$

after denoting

$$c_1 = \int_0^\infty \frac{d\eta^\alpha}{2(1 + \frac{\eta}{2})},$$

we can write

$$\int_0^\infty \left(\frac{1}{\xi} - \frac{1}{\xi(1 + \frac{k_0}{2}\xi)} \right) d\xi^\alpha = \frac{k_0}{2} \int_0^\infty \frac{d\xi^\alpha}{1 + \frac{k_0}{2}\xi} = \left(\frac{k_0}{2} \right)^{1-\alpha} \int_0^\infty \frac{d\eta^\alpha}{1 + \eta} = c_1 \left(\frac{k_0}{2} \right)^{1-\alpha} \quad (31)$$

Hence,

$$\begin{aligned}
 k_0 &= -\frac{1}{b^\alpha}c_1 + \frac{1}{b^\alpha}c \left(\frac{k_0}{2}\right)^{1-\alpha} - \frac{k_0^{1-\alpha}}{b^\alpha} \int_0^\infty \left\{ \frac{1}{e^\eta - 1} - \frac{1}{\eta(1 - \frac{\eta}{2})} \right\} d\eta^\alpha - \frac{1}{2} \int \frac{d\eta^\alpha}{1 + \frac{\eta}{2}} \cdot \frac{k_0^{1-\alpha}}{b^\alpha} \\
 &= -\frac{1}{b^\alpha}c + \frac{k_0^{1-\alpha}}{b^\alpha}c.
 \end{aligned}
 \tag{32}$$

Since k_0 is the number of particles, $b = 1/T$, and $\alpha = 1 + \gamma$, it follows that $k_0 b^\alpha$ for $\gamma > 0$ is the value of the Riemann zeta function, $\zeta(1 + \gamma)$. Therefore, $k_0^{\gamma+1}$ increases for $\gamma < 1$, and the first term of the right-hand side of equation (32) can be neglected. By setting $T_{cr} = 1$ in this asymptotic formula, we see that the function

$$\mathcal{M}(\gamma + 1) = \left(\frac{c(\gamma)}{\Gamma(\gamma + 1)} \right)^{\frac{1}{1+\gamma}}
 \tag{33}$$

can naturally be regarded as an extension of the Riemann zeta function ζ to the additional range of arguments given by $0 > \gamma \geq -1$.

Remark 5. The asymptotic behavior of formula (26) for $\mu < 0$ can be represented in the form

$$\int \frac{t^\gamma dt}{k_2 e^{-\mu k_1} e^{t/k_2} - 1} - \Gamma(\gamma + 1) \text{Li}_{\gamma+1}(e^\mu),
 \tag{34}$$

and, as $k_1 \rightarrow \infty$, $k_2 \rightarrow \infty$, and $\mu \rightarrow 0$, it passes to $c(\gamma)$.

The compressibility factor

$$Z_\gamma = -\zeta(\gamma + 2)/\mathcal{M}(\gamma + 1)$$

is subjected to a jump from $\gamma = 0$ to $\gamma < 0$. We obtain a termination of the metastable area of negative pressures. This implies the paradoxical effect of increasing density under decreasing temperature, which is actually observed experimentally (see [4], and also [5]).

In the approach under consideration, we see that the trajectory satisfies the relation

$$\mu dN = 0.
 \tag{35}$$

Thus, the new ideal gas gives discontinuous isotherms consisting of a gaseous branch and an incompressible liquid branch.

From the point of view of economics, this means that the reduction of “freedom” is carried out, first, at the expense of uniting, and then, at the expense of toughening the laws; for instance, there must be no unemployed and the number N must be preserved. From the point of view of physics, this means that, for $T > 1$, as the number N is increased, a cascade-like increase of the joining into clusters occurs, and then the jamming phenomenon can be observed (an incompressibility) in which the increase of pressure does not cause any decrease in volume.

The trajectory consisting for $T > 1$ of two intersecting straight lines on the $\{Z, P\}$ plane, the very trajectory following from number theory, is the skeleton of thermodynamics, the new ideal gas. Smoothing (filling by conjunctive tissue) of this skeleton is given by taking the interactions into account.

Remark 6. The phase transition of the first kind on the P, Z plane for $T < T_{cr}$ occurs at $P = P_{cr}$ under a modification of the density and variable chemical potential, and the phase transition of the first kind at $T < T_{cr}$ occurs on the isotherm for different pressures and different chemical potentials. In the van der Waals diagram, to the last phase transition there corresponds a passage from the gaseous branch to the liquid branch along the entire interval of metastable states, from the spinodal point on the gaseous branch to the spinodal point on the liquid branch.

To obtain a phase transition of the standard form for $T < T_{cr}$, one must find points on both the isotherms at which the chemical potentials are equal. This is a special condition of projecting to the T, P plane of two Lagrangian manifolds with boundaries (the boundary corresponds to the

spinodal) under which the Gibbs potential takes the maximal value. In other words, the chemical potential is minimized along the isotherm.

The so-called geometric quantization of these two manifolds can be carried out by means of the tunnel canonical operator, where $1/N$ serves as a small parameter. This is a diffusion of gas (see [6]).

Thus, in the case of the new ideal gas, we obtain an incompressible liquid and a nonanalytic dependence, namely, an isotherm–isobar goes from γ to γ' , whereas below γ' , for $P < 1$, there is an isotherm–isochor.

For $T > T_{\text{cr}}$, we consider isochors–isodims issuing from the critical isotherm. These are curves with constant density and constant fractional dimension γ corresponding to the line $Z = \text{const}$ intersecting with the critical isotherm. As was already mentioned above, along the interval on isotherm–isobar, the value γ changes from $\gamma = \gamma_0$ to γ' .

The smoothing for $\gamma < \gamma'$ occurs at the expense of the Zeno line, and on the isochor–isodim, at the expense of diffusion and geometric quantization of thermodynamics, we have $T = T_{\text{cr}}$ and $P < P_{\text{cr}}$ near the focal point.

If the value γ_{sum} belongs to the interval (γ, γ') , where $\gamma < \gamma'$, then $Z_\gamma = V$, where V is the volume. In this case, the relation for the densities and for the NT-internal energy enables us to evaluate an analog of the Zeno line for the mixture of two gases, and hence also to evaluate the function

$$\varphi_{\gamma_{\text{sum}}}(V/\rho_{\text{cr}})$$

and to refine, for a real gas, the relations presented in [6, Sec. 7].

5. CONCLUSION

For thermoeconomics, the suggested approach corresponds to the situation in which a united currency is introduced for two different states. For experimental physicists, the approach helps to study the relationship among different parameters of the problem and to understand in what areas one must make more detailed measurements.

This approach is especially important for computer experiments in which an additional parameter arises, namely, the step of the grid.

The multiscale features of processes related to molecular physics manifest themselves especially well in the scaling hypothesis, which is verified quite inaccurately in the model of molecular dynamics, by increasing the number of launched particles.

It is impossible to create a correct architecture [8] of computing media and environments without a deep investigation of the relationship between the computer “viscosity” (see [7]) and the mathematical analysis of “deviations” and paradoxes in laws of phenomenological thermodynamics. In [2, 3, 6, 9, 10], the “deviations” between the scaling hypothesis and the “classical” critical exponents, Einstein and Gibbs paradoxes, and other discrepancies in phenomenological thermodynamics and molecular physics were studied mathematically rigorously. These contradictions manifest themselves especially vividly in long-living metastable phenomena for the liquid phase (including those occurring under negative pressures), where the van der Waals model shows a fundamental discrepancy from the full-scale data, as well as in the area of fluids.

For this reason, the comparison of mathematical modeling for multiscale thermodynamical processes with full-scale data and data of modern computer experiments in molecular dynamics is necessary to develop hierarchical models of processes, algorithmic assembling, and architecture of supercomputers.

In the present work, we specially stress the resolution of the above contradictions by using tools of modern tropical mathematics from the standpoint of applying these solutions to the problem of mixture of different gases. Up to now, solutions of the last problem by methods of molecular dynamics were based on an empirical choice of some average interaction potential.

We suggest forecasting in order to predict results of full-scale experiments and to direct them in the desired way by using modern computer technologies.

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