

The Role of Macroinstrument and Microinstrument and of the Observable Quantities in the New Conception of Thermodynamics

V. P. Maslov

*Moscow State Institute of Electronics and Mathematics -
Higher School of Economics, 109028, Moscow, Russia*

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Abstract. In the first part of the paper, we introduce the concept of observable quantities associated with a macroinstrument measuring the density and temperature and with a microinstrument determining the radius of a molecule and its free path length, and also the relationship between these observable quantities. The concept of the number of degrees of freedom, which relates the observable quantities listed above, is generalized to the case of low temperatures. An analogy between the creation and annihilation operators for pairs (dimers) and the creation and annihilation operators for particles (molecules) is carried out. A generalization of the concept of a Bose condensate is introduced for classical molecules as an analog of an ideal liquid (without attraction). The negative pressure in the liquid is treated as holes (of exciton type) in the density of the Bose condensate. The phase transition gas-liquid is calculated for an ideal gas (without attraction). A comparison with experimental data is carried out.

In the other part of the paper, we introduce the concept of new observable quantity, namely, of a pair (a dimer), as a result of attraction between the nearest neighbors. We treat in a new way the concepts of Boyle temperature T_B (as the temperature above which the dimers disappear) and of the critical temperature T_c (below which the trimers and clusters are formed). The equation for the Zeno line is interpreted as the relation describing the dependence of the temperature on the density at which the dimers disappear. We calculate the maximal density of the liquid and also the maximal density of the holes. The law of corresponding states is derived as a result of an observation by a macrodevice which cannot distinguish between molecules of distinct gases, and a comparison of theoretical and experimental data is carried out.

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1. INTRODUCTION

The difference between readings of measuring macro- and microinstruments in thermodynamics is related to the following aspects.

1. A macroinstrument does not take into account the motions of nuclei, of electrons, and even of atoms within a molecule and regards any molecule as an individual particle. Mathematically, this corresponds to imposing rigid constraints on the elements forming the molecule. That is, we must modify those axioms of mechanics in which we consider all elementary particles and their behavior in the configuration space whose dimension is equal to the tripled number of elementary particles.

2. A macroinstrument measuring density counts the number of particles in a fragment of the volume; however, it cannot trace the movements of particles with different numbers during discrete finite time intervals. At each discrete time moment, this device counts the number of particles in the same fragment; however, it cannot notice what is the exact position of any particle indexed at the previous time moment and whether or not this particle really is within the chosen fragment. Mathematically, this means that the arithmetical law of rearrangement of summands holds. The sum does not depend on the way in which we have indexed the particles. In this sense, the laws of classical mechanics are even modified in a more substantial way.

Let us quote from the textbook [1] on quantum mechanics, where the authors define the basic property of classical mechanics: “In classical mechanics, identical particles (e.g., electrons) do not lose their ‘personality,’ despite the identity of their physical properties. Specifically, you can imagine

that the particles forming a given physical system are ‘indexed’ at some time moment and then one can trace the motion of each of the particles along its own trajectory; then the particles can be identified at any time moment. . . . In quantum mechanics, it is fundamental that there is no way to trace each of the identical particles separately and thus to distinguish them. We can say that, in quantum mechanics, identical particles completely lose their individuality” (Russian p. 252).

A macroinstrument does not keep this basic property either. Mathematically, this means that, to take this property into account, we should impose some new constraints, which are already explicitly nonholonomic, on the mechanics of many particles and, which is especially important, we should take into account the permutability of particles in the definition of density, namely, *any permutation of particles does not modify the density*.

It follows from these considerations that

1) in general, the dimension of the configuration space in thermodynamics does not match the dimension of the momentum space (the latter is associated with the number of nonholonomic constraints);

2) the entropy (in contrast to the Boltzmann–Shannon entropy) should take into account the permutability of the indices of the particles (cf. [2], §40).

Hence, for an ideal gas

$$\sum_j N_j = \sum_j G_j \bar{n}_j = N, \quad \sum_j \varepsilon_j N_j = \sum_j \varepsilon_j G_j \bar{n}_j = E, \quad (1)$$

$$\frac{\partial}{\partial \bar{n}_j} (S + \alpha N + \beta E) = 0, \quad (2)$$

where \bar{n}_j stands for the average number of particles in each of the G_j states of the j th group and α and β are some constants (see [2], the footnote on p. 184, and also [4] and [5]).

The entropy must be of the form

$$S = \sum_j \{(G_j + N_j) \log(G_j + N_j) - N_j \log N_j - G_j \log G_j\}, \quad (3)$$

$$S = \sum_j G_j [(1 + \bar{n}_j) \log(1 + \bar{n}_j) - \bar{n}_j \log \bar{n}_j]. \quad (4)$$

In other words, the entropy has exactly the same form as in the Bose–Einstein quantum case.

We have noted above that a macroinstrument and its measurements force mathematicians to reorganize even the axioms of classical mechanics. However, mathematicians are forced to do so by entering the corresponding small parameters and passing to the related limits. A macroinstrument and its measurements still reduce the time spent to perform constructions of this kind. However, when one speaks of the axioms of thermodynamics, which is based on laws derived by great physicists who used ancient experiments conducted on Earth, it then turns out that the above considerations modify the classical concept of thermodynamics completely. Meanwhile, microinstruments¹ also play a role in classical thermodynamics; they enable one to calculate the dimension related to the number of atoms in the molecule.

In the mathematical literature, as a rule, the number of degrees of freedom coincides with the number of independent generalized coordinates. However, these notions are distinct in the standard thermodynamics, because the volume is three-dimensional, which is established by the macrodevice, whereas the number of degrees of freedom is related to the number of atoms in a molecule and is measured by the microdevice. It turns out that the number of degrees of freedom coincides with the dimension of the generalized Bose gas which is regarded as a distribution of a classical gas.

Landau and Lifshitz notice this fact for the three-dimensional Bose gas. They write that these equations ($PV^{5/3} = \text{const}$) coincide with the equations of the adiabatic line for an ordinary

¹In mathematics and mechanics, the difference between micro- and macro-observations is defined as follows: “the radius a of a molecule is much less than the typical length of the vessel (provided that the shape of the vessel is given)”, i.e., there are two scales in the problem, which correspond to macro- and microinstruments.

monatomic gas. “However, we stress,” the authors write further, “that the exponents in the formulas $VT^{3/2} = \text{const}$ and $PV^{5/3} = \text{const}$ are not related now to the ratio of specific heat capacities (since the relations $c_p/c_v = 5/3$ and $c_p - c_v = 1$ fail to hold)” [2, 187].

One can show in a quite similar way that, for the five-dimensional and six-dimensional Bose gas, the “Poisson adiabatic line” coincides with the Poisson adiabat for the two-atomic and three-atomic molecule (see [2], §47, Diatomic gas with molecules of different atoms. Rotation of molecules). With regard to the above stipulation, as $\mu \rightarrow -\infty$, we obtain precisely both the condition $c_p - c_v = 1$ and the ratio c_p/c_v coinciding with relations well known in the old thermodynamics.

According to [2], the number of degrees of freedom decreases as the temperature decreases. This means that this number depends on energy, and, since the speeds of gas particles are different, it follows that the number of degrees of freedom of these particles is different in general. Averaging over all speeds gives a fractional number of degrees of freedom in the general case.

Remark 1. Let us explain the following experimental fact. In some cases, the number of degrees of freedom for diatomic and polyatomic molecules is an integer. This fact manifests itself when calculating the heat capacity C_V . In our opinion, this happens because the intramolecular communications (the distances between the atoms of the molecule) are very hard, and, when the temperature increases, no new degrees of freedom arise. Generally speaking, the number of degrees of freedom fundamentally depends on the energy of the molecules, and the energy of different molecules of the same gas is different, and, apparently, to the average energy (the temperature) there must correspond the average number of degrees of freedom, which is hence must be non-integer. However, on one hand, tight connections enable one to excite almost all molecules for a sufficiently high (room) temperature and, on the other hand, to give the molecules no possibility to excite new degrees of freedom (e.g., the vibrational ones). If the connections are not so rigid, then the number of degrees of freedom depends on temperature, and hence on energy, and is not an integer in general. This is clear from the comparison of the values of the heat capacity C_V with the experiment: for hydrogen sulfide with three atoms, the theory gives 5.96, and the experiment 6.08, for carbon dioxide, the experiment gives a greater value $C_V = 6.75$ ($T = 15C$, $P = 1\text{atm}$), and, for carbon disulfide, the value is almost two times larger, namely, 9.77. In the case of diatomic molecules, say, for nitrogen, the theory gives 4.967 and the experiment shows 4.93; for the chlorine, the value is almost 20% higher, namely, 5.93, etc.

We have already said above that the number of degrees of freedom is equal to the dimension of the Bose–Einstein distribution.

2. A NEW IDEAL GAS AND A NEW IDEAL LIQUID AS OBSERVABLE QUANTITIES

2.1. The number of degrees of freedom for $T \leq T_c$ and $P \leq P_c$

Let us now proceed with finding the number of degrees of freedom for a temperature which is lower than the critical one, $T < T_c$.

The Maxwell–Boltzmann equation for the ideal gas is of the form

$$PV = NT, \quad (5)$$

where P stands for the pressure, V for the volume, N for the number of particles, and T for the temperature.

Denote by Z the dimensionless quantity $Z = \frac{PV}{NT}$, which is called the *compressibility factor*. Equation (5) can be represented in the form $Z = 1$. Let us express the Bose–Einstein distribution for the fractional dimension D using polylogarithms.

Represent the thermodynamic potential of the Bose gas of the fractional dimension $D = 2(1+\gamma)$ in the form

$$\Omega(\mu, T) = (Cm)^{1+\gamma} V \frac{T^{2+\gamma}}{\Gamma(2+\gamma)} \int_0^\infty \frac{t^{1+\gamma} dt}{(e^t/a) - 1} = -T^{2+\gamma} (Cm)^{1+\gamma} V \text{Li}_{2+\gamma}(a), \quad (6)$$

where T stands for the temperature, m for the mass, C is a constant, $a = \exp(\mu/T)$ is the activity, μ is the chemical potential, and Γ stands for the Euler gamma function.

The function $\text{Li}_s(a)$ introduced in (6) is referred to as a polylogarithm and is defined by the rule

$$\text{Li}_s(x) = \frac{1}{\Gamma(s)} \int_0^\infty \frac{t^{s-1}}{(e^t/x) - 1}, \quad \text{Li}_s(1) = \zeta(s), \quad (7)$$

where $\zeta(s)$ stands for the Riemann zeta function.

To pass to the dimensionless units, we introduce the temperature T_r in such a way that $T = T_r T_c$.

The expressions for the dimensionless pressure $P_r = P/P_c$ and for the number of particles N that correspond to the thermodynamic potential (6) are of the form

$$P_r = \frac{T_r^{2+\gamma} \text{Li}_{2+\gamma}(a)}{\zeta(2+\gamma)}, \quad (8)$$

$$N = T_r^{1+\gamma} \text{Li}_{1+\gamma}(a). \quad (9)$$

We have (for the definition of γ_c , see below)

$$\Omega' = -T_r^{2+\gamma} (Cm)^{\gamma_c - \gamma} V \text{Li}_{2+\gamma}(a). \quad (10)$$

The following formula can thus be obtained for the compressibility factor Z :

$$Z = \frac{\text{Li}_{2+\gamma}(a)}{\text{Li}_{1+\gamma}(a)}. \quad (11)$$

In particular, for $a = 1$ (i.e., for $\mu = 0$), we have

$$Z = \frac{\zeta(\gamma + 2)}{\zeta(\gamma + 1)}, \quad (12)$$

where ζ stands for the Riemann zeta function.

As is well known, in the Bose–Einstein theory, the value $\mu = 0$ corresponds to the so-called degeneration of the Bose gas.

For a classical gas satisfying the same relations, the *degeneration coincides with the critical point* $T = T_c$, $P = P_c$, and $Z = Z_c$. Consequently, one can write $\gamma = \gamma_c$ for $Z = Z_c$ in (12), and to every pure classical gas there corresponds its own value of γ_c .

The entropy in the dimension $D = 2\gamma + 2$ can be evaluated in the standard way. The great thermodynamical potential is considered,

$$\Omega = -PV = -\frac{VT}{\Lambda^{2(1+\gamma)}} \cdot \frac{1}{\Gamma(2+\gamma)} \int_0^\infty \frac{t^{1+\gamma} dt}{(e^t/a) - 1} = \frac{-VT^{2+\gamma}}{\Lambda'^{2(1+\gamma)}} \text{Li}_{2+\gamma}(a),$$

where $\Lambda' = \text{const}/(2\pi m)^{1/2}$, the dimension D is equal to $2\gamma + 2$, T stands for the temperature, and $a = e^{\mu/T}$ for the activity.

The number of particles is

$$N = -\frac{\partial \Omega}{\partial \mu} = \frac{T^{1+\gamma}}{\Lambda'^{2(1+\gamma)}} \text{Li}_{1+\gamma}(a).$$

The compressibility factor is

$$Z = \frac{PV}{NT} = \frac{\text{Li}_{2+\gamma}(a)}{\text{Li}_{1+\gamma}(a)}.$$

Let us evaluate the entropy,

$$\begin{aligned} S &= - \left(\frac{\partial \Omega}{\partial T} \right)_{V, \mu} = (2 + \gamma) \frac{VT^{1+\gamma}}{\Lambda^{2(1+\gamma)}} \text{Li}_{2+\gamma}(a) - \frac{VT^{1+\gamma}}{\Lambda^{2(1+\gamma)}} \text{Li}_{1+\gamma}(a) \frac{\mu}{T} \\ &= \frac{VT^{1+\gamma}}{\Lambda^{2(1+\gamma)}} \left[(2 + \gamma) \text{Li}_{1+\gamma}(a) - \text{Li}_{1+\gamma}(a) \frac{\mu}{T} \right]. \end{aligned}$$

For $\mu = 0$, $T_r = T/T_c$, and $P_r = P/P_c$, the specific entropy is equal to

$$\frac{S}{V} \Big|_{\mu=0, T_r=1} = \frac{\partial \Omega_\gamma^{id}}{\partial T} = (2 + \gamma) \zeta(2 + \gamma). \quad (13)$$

E. M. Apfel'baum [Apfelbaum] and V. S. Vorob'ev [3] compared the Bose distributions of fractional dimension $D = 2\gamma_c + 2$ in the (P, V) diagram with the experimental critical isotherms for various gases. We present these graphs in Figs. 1–5. In Fig. 5A, the graphs for the nitrogen and oxygen are shown, which have been constructed by Professor V. S. Vorob'ev.

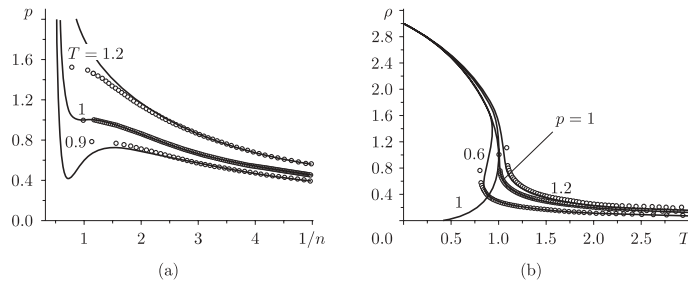


Fig. 1. (a) Isotherms of pressure for the van der Waals equation are shown by solid lines. The lines formed by circles are constructed from computations for $\gamma = 0.312$ (i.e., for the ideal “Bose gas”), $Z_{cr} = 3/8$, $p = P/P_c$, and $n = N/N_c$. (b) Isobars of density for the van der Waals equation are shown by solid lines. Line 1 is the binodal. The circles correspond to isobars of the “Bose gas” for $\gamma = 0.312$.

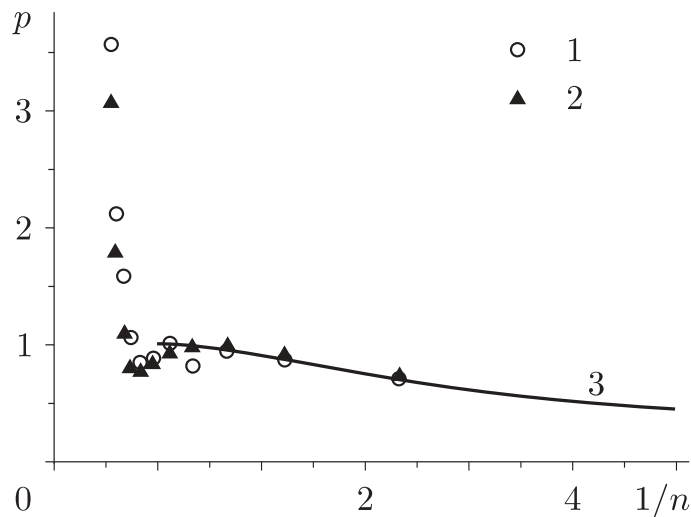


Fig. 2. Critical isotherms for the Lennard–Jones system. Symbols 1 and 2 correspond to numerical calculations. Line 3 corresponds to the ideal Bose gas for $\gamma = 0.24$.

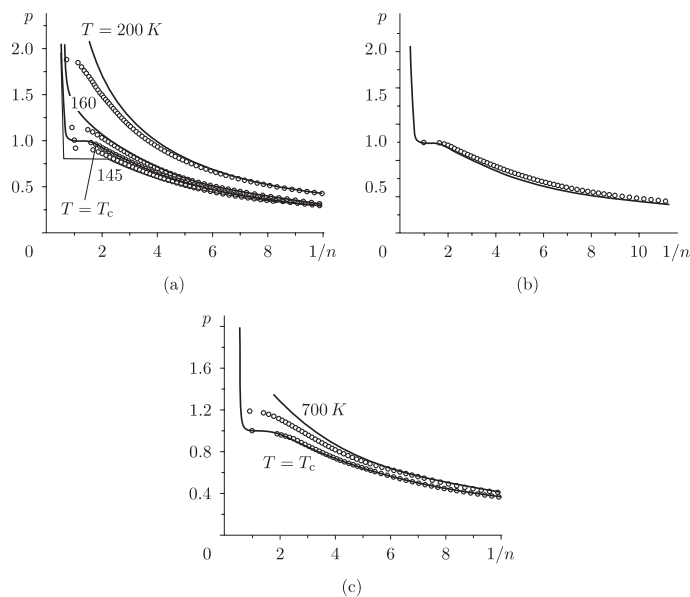


Fig. 3. (a) Isotherms for argon. The solid lines correspond to experimental data. The line formed by circles is constructed in accordance with the isotherm of the ideal “Bose gas”; $Z_{cr} = \frac{\zeta(\gamma+2)}{\zeta(\gamma+1)} = 0.29$, $p = P/P_c$, and $n = N/N_c$.
 (b) The same for water, $Z_{cr} = 0.23$.
 (c) The same for copper, $Z_{cr} = 0.39$.

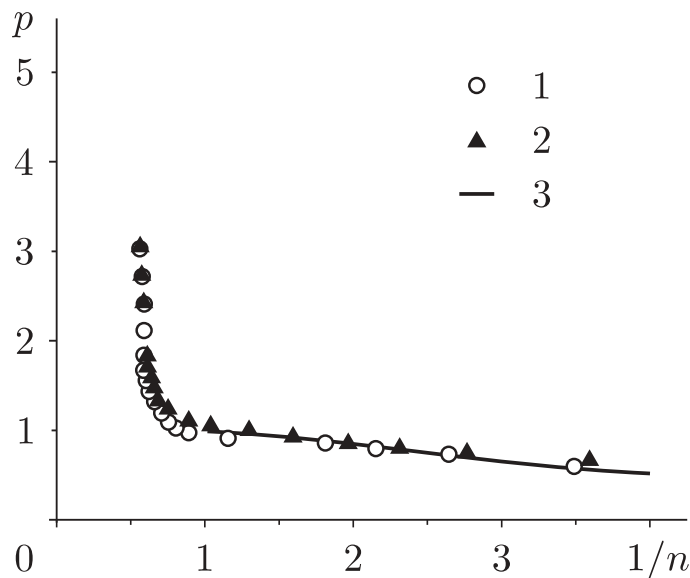


Fig. 4. Isotherms for water. Symbols 1 and 2 correspond to experimental data, and line 3 corresponds to the computation for the Bose gas.

2.2. Bose condensate as an observable quantity in classical thermodynamics

We shall show that the Bose condensate in classical thermodynamics is the condensate of gas (vapor) into liquid (in contrast to the statement presented in the manual [2] in the footnote on p. 199).

Example 1. Consider the example given by a famous theorem in number theory, namely, the solution of an ancient problem, which has the Latin title “partitio numerorum.” This task

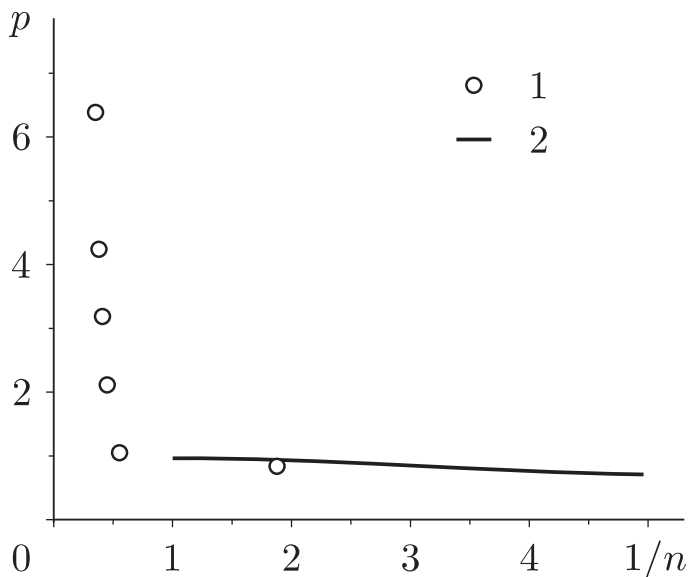


Fig. 5. Critical isotherms for mercury. Symbols 1 and 2 correspond to experimental data, and line 3 corresponds to the computation for the Bose gas.

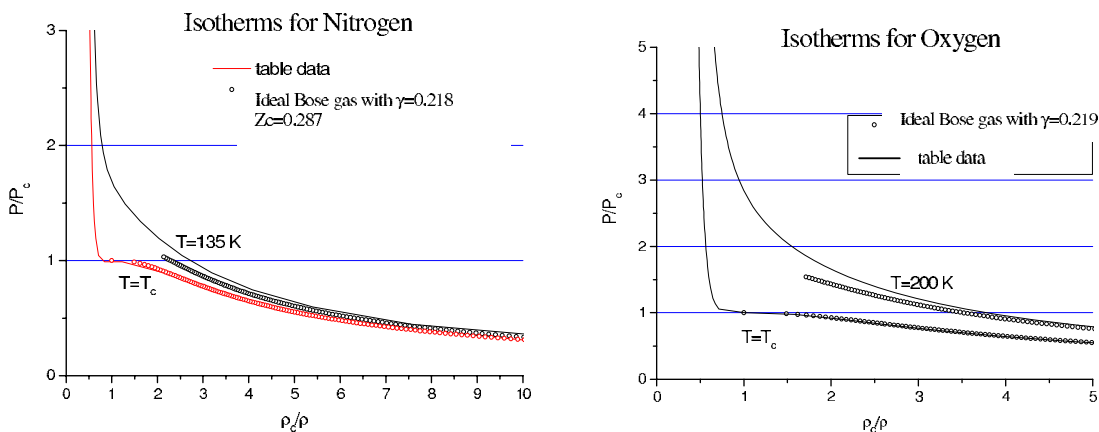


Fig. 5A. 5A-1. Isotherms for nitrogen. 5A-2. Isotherms for oxygen.

involves an integer M which is decomposed into N terms, for example, if $M = 5$ and $N = 2$, then $5 = 1 + 4 = 2 + 3$, which gives two solutions to the problem, $\mathcal{M} = 2$.

If $M = 10^{23}$ and $N = 1$, then the decomposition has only one version, and $\mathcal{M} = 1$. If $M = 10^{23}$ and $N = 10^{23}$, then there is also only one version of decomposition, namely, the sum of ones, i.e., $\mathcal{M} = 1$.

Obviously, there is a number N_c for a fixed M such that the number of versions of the decomposition, \mathcal{M} , is maximal possible (this number is not unique in general). The number $\log_2 \mathcal{M}$ is referred to as the *Hartley entropy*. At the point at which \mathcal{M} reaches its maximum, there is a maximum entropy.

Let a partition $M = a_1 + \dots + a_N$ of M into N summands be given. Denote by N_j the number of summands on the right-hand side that are precisely equal to j .

Then the total number of summands is $\sum_j N_j$, and this number is equal to N , since we know that the total number of summands is N . Further, the sum of the parts equal to j is jN_j , since there are N_j summands, and then the sum of all summands can be obtained by summing these

expressions over all possible j , i.e., $\sum_j jN_j$, and this sum is equal to M . Namely,

$$\sum_{i=1}^{\infty} N_i = N, \quad \sum_{i=1}^{\infty} iN_i = M. \quad (14)$$

The very nonuniqueness of the above maximum and an uncertainty concerning the number of the maxima enabled Erdős to obtain results with accuracy up to $o(\sqrt{M})$ only.

Thus, the Erdős theorem holds for the system of two Diophantine equations

$$\sum_{i=1}^{\infty} N_i = N, \quad \sum_{i=1}^{\infty} iN_i = M. \quad (15)$$

The maximum number of solutions of the system is achieved provided that the following relation holds:

$$N_c = \beta^{-1} M_c^{1/2} \log M_c + \alpha M_c^{1/2} + o(M_c^{1/2}), \quad \beta = \pi\sqrt{2/3}, \quad (16)$$

and the coefficient α is defined by the formula $\beta/2 = e^{-\alpha\beta/2}$.

If one increases the number N in problem (15) and keeps the number M constant, then the number of solutions decreases. If the sums in (15) are counted from zero rather than from one, i.e.,

$$\sum_{i=0}^{\infty} iN_i = (M - N), \quad \sum_{i=0}^{\infty} N_i = N, \quad (17)$$

then the number of solutions does not decrease and remains constant.

Let us explain this fact. The Erdős–Lehner problem [6] is to decompose a number M_c into $N \leq N_c$ summands.

The decomposition of the number 5 into two summands has two versions. If we include also 0, then we obtain three versions, $5+0 = 3+2 = 4+1$. Thus, the inclusion of zero gives the opportunity to say that we decompose the number into $k \leq n$ summands. Indeed, the expansion of the number 5 into 3 summands includes all previous versions: $5 + 0 + 0$, $3 + 2 + 0$, and $4+1 + 0$ and adds new options that do not contain zero.

Here the maximum does not change much [6]; however, the number of options cannot decrease, because the zeros enable the maximum to remain constant, and the entropy never decreases; after reaching the maximum, it becomes constant. This very remarkable property of entropy enables us to construct a general unbounded probability theory [7]. In physics, the effect is identical to the so-called phenomenon of Bose condensate.

Let us pose the following question: what is the difference between arithmetic, together with the problem of “partitio numerorum,” and the Boltzmann–Shannon statistics? If we assume that $4 + 1$ and $1 + 4$ are two different versions, then we obtain the Boltzmann–Shannon statistics. The number of versions of decomposition, \mathcal{M} , is growing rapidly. Thus, the “noncommutativity” of the addition gives additionally a huge number of versions of decomposition, and the Hartley entropy (which is equal to the logarithm of the number of versions) coincides with the Boltzmann–Shannon entropy.

Therefore, we have proved that, if we add zero to the family of possible summands and decompose a number M into N summands, then this is equivalent to solving equations (17), i.e., to imposing relations for the number of particles and for energy. Here the number of zeros increases drastically; if $M = 5$, then, for $N > 3$, the number of zeros is 22. This is the very Bose condensate. However, the number of ones is also large, although it is twice smaller than the number of zeros.

Example 2. Suppose that two persons toss two identical coins simultaneously. The following events are equiprobable: (heads, heads), (tails, tails), (heads, tails), (tails, heads). Let us assume that we cannot understand who had tossed each of the coins after the coins fell. Then the number of possible versions is three, namely, (heads, heads), (tails, tails), and (heads, tails). If there are many tosses, then the cluster of (eagle, tails) grows. It consists of mixed coins of the two tossing persons.

This phenomenon is obviously not surprising. Similarly, the indistinguishability of particles by a device leads to a cluster-fluctuation which is called the Bose condensate.

It is very visible to consider the Bose condensate as the number of zeros; however, this is inaccurate. The Bose condensate occurs in a neighborhood of a point at which the energy vanishes rather than at the point itself. Nevertheless, if one writes $\rho_0\delta(\mathbf{k})$ (where ρ_0 stands for the density and the vector \mathbf{k} is the momentum) for the Bose condensate at rest, then this notation is true, because the density is the limit

$$\rho_0 = \lim_{N \rightarrow \infty, V \rightarrow \infty} \frac{Nm}{V},$$

where N stands for the number of particles, V for the volume, and m for the mass of the particle. This means that, as $N \rightarrow \infty$, the bell-shaped function near the zero energy is converted to the δ function.

By an ideal (or perfect) liquid we mean a liquid without attraction and without any surface tension. This is a liquid which can exist for a positive pressure only together with a saturated steam.

In this case, the perfect liquid is the result of an optical illusion, and this “perfect liquid” is the same ideal gas in the condensate, with another density. It can be described, as in the case of a consideration of a Bose condensate, in the form $\rho_0\delta(\mathbf{k})$, where ρ_0 stands for the density of the condensate. It cannot exist without a volume trap, which is similar to the case in which a container with gas has a hole, and there is a vacuum outside the vessel, in which case this liquid, which looks as if it is boiled, is going away together with the gas. The mean speed of the particles inside the liquid is the same as the mean speed of the gas particles. This corresponds to the condition that the temperature in the system “liquid–saturated steam” is the same in the liquid and in the gas. The liquid in a closed vessel is a fluctuation standing at a fixed place ($\delta(\mathbf{k})$), or, speaking in a simpler way, this liquid is a “resting” Bose condensate (cf. [8, 204]).

Small crystals that occur in a supersaturated solution coincide with the Bose condensate only if they are not composed of mutually connected particles, and, moreover, if the particles are continuously exchanged with the particles in the solution; moreover, the small crystals, as solids, are an optical illusion, namely, we simply do not see that the particles of crystals are permanently transposed with particles of the solution. In other words, this is by no means a crystal, this is a fluctuation; however, this fluctuation is relatively immobile.

Thus, the Bose condensate for classical particles represents some “special density fluctuations;” only this, and nothing more. One can talk about the density in a “special cluster fluctuation” of a part of our vessel with gas. If we speak of the density in this cluster only, this means that (as in the example of a small volume with one million of particles) one cannot speak of the number of particles that are placed in the cluster as if they are frozen and do not move. This is only an appearance, and all of the particles or a part of them can be replaced in a minute by another ones, and the indexing inside the “fluctuation” cluster can change every minute. At the next instant, the picture can be quite the same, but other particles will be involved.

We speak about some fragment of the volume. In fact, the particles that are more concentrated can be spread out over the entire vessel. However, if there is at least a little gravity of the Earth, then the fluctuations with more concentrated particles accumulate near the bottom. If we consider a vessel with gas in the form of a perfectly reflecting sphere (see [9–12]), then, due to the repulsive force occurring at the border, fluctuations of this kind are located near the center of the ball.

Let us repeat once again that the only fact which can be guaranteed by the generalized theory of Bose condensate is that there will be a high density of particles at the bottom.

Example 3. Let a gas be contained in a closed vessel at a room temperature, and let the gas be almost satisfying the Clausius relation

$$P = \rho T. \tag{18}$$

We cool the vessel down to a temperature $T = 0$. At some temperature $T \geq T_0$, a liquid is formed. The temperature T_0 is referred to as the dew point. According to the standard conception, the fluctuations above the temperature of the dew point are of the order of \sqrt{N} . After the formation of liquid, the gas, which is called a saturated steam in the physical literature, also satisfies relation (18).

It is quite rarefied. According to the van der Waals model, there are no singularities at the dew point under the gas-liquid passage (on the so-called binodal). According to experimental data, there are no large fluctuations either in the usual sense at the dew point.

Finally, the most important thing. The experiment shows that, at $T = T_0$, the gas is rarefied, and it remains an ideal gas.

There is, however, a fluctuation of the type of a stationary Bose–Einstein condensate. In this fluctuation, the molecules by themselves placed inside this fluctuational fragment can possibly move with the same velocities as those of the gas molecules and, if it were possible to enumerate them, then the numbers will be changed very quickly. If shall refer to this fluctuation (of the form of the Bose-Einstein condensation) as liquid, then actual molecules of the liquid move in it with the same speeds as the gas molecules (of the “saturated vapor”).

To represent this picture in a more visible way, imagine a bunting which winds from one roller to the other. Between the rollers, under the material, a strong wind blows from a hose. We see a “hump” is formed between the rollers; however, it can be assumed that we do not see that the bunting moves.

Nevertheless, as the density of the Bose condensate increases, our macroinstrument can fix the bound of the density and show us that there is a more dense phase and a less dense phase. Hence, only the original macroinstrument can show us the bound of this abstract liquid, i.e., of the second phase.

If liquid droplets occur below the temperature of the “dew point,” then the droplets are spherical, even under the presence of the gravity of the Earth (physicists refer to the very gravity, as a rule, when claiming that the border between gas and liquid is flat). The pressures in the droplet and in the gas (the saturated vapor) are different, due to the surface tension.

Therefore, the main rule of the equilibrium “vapor-liquid,” namely, the coincidence of the pressures, really holds at the dew point only if we neglect the surface tension, and thus neglect the attraction of liquid molecules, because these two effects are inseparably linked with each other. Our concept of a new ideal gas is based on the very assumption on the absence of attraction between the molecules.

The picture in which the attraction and the surface tension play no role can be observed in experiments if the temperature is equal to the temperature T_0 of the gas-liquid transition (i.e., at a point of the “binodal”) and T_0 is still greater than the temperature at which a droplet of critical radius has been already formed. Then, at $T = T_0$, the incipient drops spontaneously shrink and occur at another point. These drops cannot live without the surrounding saturated vapor; one can see these drops but cannot feel them.

If the vessel is spherical and the mean free path is comparable to the size of the vessel (similar to the so-called Knudsen criterion; see [9–12]), then the probability of such a virtual drop is larger at the center of the vessel.

In this case, if we make the labelling of several molecules by launching few isotopes which can be traced, then these isotopes will pass freely through the liquid to vapor and back, and they will form a denser structure near the center of the ball, in such a way that, when illuminated by parallel rays, it will provide a shade. However, it is impossible to take this drop from the gas medium. One can see an ideal liquid but cannot feel it². Possibly it is better to refer to it as a “virtual liquid.”

This approach is unusual for the majority of physicists. Although everyone knows that, say, when photons are collected at a focus at which their “density” is high, then it is impossible to separate the focus from the “photon medium.”

A mathematical analog of the quantum Bose condensate for a classical gas is a liquid without attraction in which the speeds of the molecules are approximately the same as the speeds of the molecules in the saturated vapor. The attraction between molecules results in a significant correction provided that the radius of a drop is greater than the critical one; however, this correction abolishes the conditions of the vapor–liquid equilibrium for the pressure. Therefore, the problem must be divided into two separate problems, namely, 1) an ideal gas and a perfect liquid without attraction, and 2) the consideration of the attraction for the case in which the decay into two phases has already been carried out and the radius of the drop exceeds the critical value.

²One cannot drink it but can breathe it in.

2.3. Asymptotic continuation of a perfect liquid to the second sheet as the volume of the liquid increases

The gas spinodal, which is defined in a new way as the locus of isotherms of a new ideal gas, is formed at the maximum entropy at the points at which the chemical potential μ vanishes.

Therefore, on the diagram (Z, P_r) , the spinodal is a segment $P_r \leq 1$, $Z = Z_c$ (in the case of the van der Waals normalization $T_r = T/T_c$ and $P_r = P/P_c$). For $T_r \leq 1$, the Bose condensate occurs and, consequently, for the liquid phase on the spinodal, the quantity $N = T_r^{\gamma_c+1} \zeta(\gamma_c + 1)$ remains constant on the liquid isotherm. This means that the isotherm of the liquid phase that corresponds to a temperature T is given by

$$Z = \frac{P_r}{T_r N} = \frac{P_r}{T_r^{\gamma_c+2} \zeta(\gamma_c + 1)}. \quad (19)$$

All isotherms of the liquid phase (including the critical isotherm at $T_r = 1$) pass through the origin $Z = 0$, $P_r = 0$ and then fall into the negative region (or to the second sheet). The point $Z = 0$ corresponds to the parameter $\gamma = 0$, and hence to the continuation to $\gamma < 0$, since, for $\mu = 0$, the pressure

$$P_r = T_r^{2+\gamma} \frac{\zeta(2+\gamma)}{\zeta(2+\gamma_c)} \quad (20)$$

can be extended to $0 > \gamma > -1$.

We shall see below that the value of Z as $\mu/T \rightarrow o(1/\log N)$ is also positive, and therefore the spinodal for $0 > \gamma > -1$ gives another sheet on the diagram (Z, P) (the second one); it is more convenient to take this sheet onto the negative quadrant.

Under the assumption that the transition to the liquid phase is not carried out for $T = 1$, we equate the chemical potentials μ and $\tilde{\mu}$ for the "liquid" and "gaseous" phase on the isotherm $T = 1$ (this fact is proved below).

After this, we find the point μ which is the point of transition to the "liquid" phase for $T < 1$ by equating the chemical potentials of the "liquid" and "gaseous" phase.

In this section, we find the point of the isotherm-isochoire of the liquid as the quantity $\varkappa = -\mu/T$ slowly tends to zero.

First of all, we take into account the fact that N_c is finite, although it is large, and hence we are to use a parastatistical correction. Recall the relation

$$\Omega = -\Lambda^{\gamma_c-\gamma} T \sum_k \log \left(\frac{1 - \exp \frac{\mu - \varepsilon_k}{T} N}{1 - \exp \frac{\mu - \varepsilon_k}{T}} \right), \quad \Lambda = Cm, \quad (21)$$

for the Ω -potential.

Applying the Euler–Maclaurin with regard to the parameter γ , we obtain

$$\sum_{j=1}^n \left(\frac{j^\gamma}{e^{bj+\varkappa} - 1} - \frac{kj^\gamma}{e^{bkj+\varkappa}} \right) = \frac{1}{\alpha} \int_0^\infty \left(\frac{1}{e^{bx+\varkappa} - 1} - \frac{k}{e^{kx+\varkappa} - 1} \right) dx^\alpha + R,$$

where $\alpha = \gamma + 1$, $k = N$, and $b = 1/T$. Here the remainder R satisfies the bound

$$|R| \leq \frac{1}{\alpha} \int_0^\infty |f'(x)| dx^\alpha, \quad \text{where } f(x) = \frac{1}{e^{bx+\varkappa} - 1} - \frac{k}{e^{kx+\varkappa} - 1}.$$

Evaluating the derivative, we see that

$$f'(x) = \frac{bk^2 e^{k(bx+\varkappa)}}{(e^{k(bx+\varkappa)} - 1)^2} - \frac{be^{bx+\varkappa}}{(e^{bx+\varkappa} - 1)^2}, \quad |R| \leq \frac{1}{\alpha} \int_0^\infty \left| \frac{k^2 e^{k(y+\varkappa)}}{(e^{k(y+\varkappa)} - 1)^2} - \frac{e^{y+\varkappa}}{(e^{y+\varkappa} - 1)^2} \right| dy^\alpha. \quad (22)$$

We also have [13, 14]

$$\frac{e^y}{(e^y - 1)^2} = \frac{1}{y^2} + \psi(y), \quad \text{where } \psi(y) \text{ is smooth and } |\psi(y)| \leq C(1 + |y|)^{-2}.$$

Substituting this formula into (22), we obtain

$$|R| \leq \frac{1}{\alpha} \int_0^\infty |k^2 \psi(k(y + \varkappa)) - \psi(y + \varkappa)| dy^\alpha \leq k^{2-\alpha} \int_{k\varkappa}^\infty |\psi(y)| dy^\alpha + \int_\varkappa^\infty |\psi(y)| dy \leq \frac{Ck^{2-\alpha}}{1 + (k\varkappa)^{2-\alpha}}$$

with some constant C . For example, if $\varkappa \sim (\log k)^{-1/4}$, then $|R|$ admits the estimate $|R| \sim O((\log k)^{(2-\alpha)/4})$. Consequently, $k = N_c$ and $T = T_c$, and we obtain the following formula for the integral with $\mu = 0$:

$$M = \frac{\Lambda^{\gamma_c - \gamma}}{\alpha \Gamma(\gamma + 2)} \int \frac{\xi d\xi^\alpha}{e^{b\xi} - 1} = \frac{\Lambda^{\gamma_c - \gamma}}{b^{1+\alpha}} \int_0^\infty \frac{\eta d\eta^\alpha}{e^\eta - 1},$$

where $\alpha = \gamma + 1$. Hence,

$$b = \frac{1}{M^{1/(1+\alpha)}} \left(\frac{\Lambda^{\gamma_c - \gamma}}{\alpha \Gamma(\gamma + 2)} \int_0^\infty \frac{\xi d\xi^\alpha}{e^\xi - 1} \right)^{1/(1+\alpha)}.$$

We obtain (see [15])

$$\begin{aligned} \int_0^\infty \left\{ \frac{1}{e^{b\xi} - 1} - \frac{k}{e^{kb\xi} - 1} \right\} d\xi^\alpha &= \frac{1}{b^\alpha} \int_0^\infty \left(\frac{1}{e^\xi - 1} - \frac{1}{\xi} \right) d\xi^\alpha \\ &+ \frac{1}{b^\alpha} \int_0^\infty \left(\frac{1}{\xi} - \frac{1}{\xi(1 + (k/2)\xi)} \right) d\xi^\alpha - \frac{k^{1-\alpha}}{b^\alpha} \int_0^\infty \left\{ \frac{k^\alpha}{e^{k\xi} - 1} - \frac{k^\alpha}{k\xi(1 + (k/2)\xi)} \right\} d\xi^\alpha \\ &= \frac{c(\gamma)}{b^\alpha} (k^{1-\alpha} - 1). \end{aligned}$$

Write $k = N|_{\tilde{\mu}/T=o(1)}$,

$$N|_{\tilde{\mu}/T=o(1)} = (\Lambda^{\gamma_c - \gamma} c(\gamma))^{1/(1+\gamma)} T, \quad \text{where } c(\gamma) = \int_0^\infty \left(\frac{1}{\xi} - \frac{1}{e^\xi - 1} \right) \xi^\gamma d\xi. \quad (23)$$

The relation $N = T_r^{\gamma_c + 1} \zeta(\gamma_c + 1)$ meets the linear relation $N = A(\gamma)T_r$, where

$$A(\gamma) = (\Lambda^{\gamma_c - \gamma} c(\gamma))^{1/(1+\gamma)}$$

for $P < 0$.

We can make the normalization of activity a at the point T_c , and we can find a_0 by matching the liquid and gaseous branches at T_c for the pressure, in order to prevent the phase transition on the critical isotherm at $T_r = 1$.

In what follows, we normalize the activity for $T_r < 1$ with respect to the value of a_0 computed below. Then the chemical potentials (in thermodynamics, the thermodynamic Gibbs potentials for the liquid and gaseous branches) coincide, and therefore there can be no phase transition “gas-liquid” at $T_r = 1$.

Now, for the isochore-isotherm of the “incompressible liquid” to take place, we must construct it with regard to the relation $N_c = \zeta(\gamma_c + 1)$, namely, $N(T_r) = T_r^{\gamma_c + 1} \zeta(\gamma_c + 1)$. We obtain the value $\gamma(T_r)$ from the implicit equation $A(\gamma) = T_r^{\gamma_c} \zeta(\gamma_c + 1)$.

Thus, for each $T_r < 1$, we find the spinodal curve (i.e., the points at which the approximate relation $\tilde{\mu} \sim T_r(\log N(T_r))^{-1/4}$ holds) in the domain of negative γ [15],

$$\Lambda^{(\gamma-\gamma_c)/(1+\gamma)} c(\gamma)^{1/(1+\gamma)} = T_r^{\gamma_c} \zeta(\gamma_c + 1), \quad (24)$$

We choose the least value of γ (it has the largest absolute value) which is one of the two solutions of equation (24) and denote it by $\gamma(T_r)$. In particular, for $T_r = 1$, we write $\gamma_0 = \gamma(1)$.

Let $a_g = e^{-\mu/T}$ be the activity of the gas and $a_l = e^{-\tilde{\mu}/T}$ the activity of the liquid. We present the condition for the coincidence of M and of the activities at the point of the phase transition,

$$T_r^{\gamma_c} \text{Li}_{2+\gamma_c}(a_g) = \Lambda^{|\gamma(T_r)|+\gamma_c} T_r^{-|\gamma(T_r)|} \text{Li}_{2-|\gamma(T_r)|}(a_l/a_0), \quad (25)$$

$$\frac{\Lambda^{\gamma_c-\gamma_0}}{\zeta(2+\gamma_c)} \text{Li}_{2+\gamma_0}(a_0) = 1, \quad a_g = \frac{a_l}{a_0}. \quad (26)$$

These two equations determine the value of the chemical potential $\mu = \tilde{\mu} = T \log a_g$ at which the phase transition of the “gas” into the “liquid” occurs.

Definition. We refer to the equation $a_g = a_l/a_0$ as the normalization of the activity on the critical isotherm.

Let $T_0 = \min_{-1 < \gamma < 0} A(\gamma)$. Thus, for every T , $T_0 < T < T_c$, we obtain a value of the reduced activity of the liquid $a_r = a_l/a_0$ (a_l stands for the activity of the liquid) that corresponds to the van der Waals normalization.

Remark 2. In thermodynamics, the critical values T_c , P_c , and ρ_c are evaluated experimentally for almost all gases, and therefore the critical number of degrees of freedom can be set in advance. The parameter $\lambda = 1/\Lambda$ ($1.6 < \lambda < 3$, $T_r > 1/3$) is defined by the coincidence of the binodal at the triple point obtained from the experiment.

2.4. Holes in the Bose condensate as observable quantities. The maximum density of holes

The molecules of an ideal gas can be thought of as tiny balls. Let us imagine holes, excitons in glass, also as balls which are empty, without the substance of a molecule. Obviously, if one mixes these balls in a glass in a chaotic way, then the chaos in the glass becomes increased. This means that the entropy increases in the presence of holes. Therefore, to achieve the maximum of the entropy, we must also additionally mix holes into this glass.

In our conception, holes occur for $\gamma < 0$.

In the ideal gas model, we ignore the attraction, and this means that, when “stretching” the liquid, which results in holes, the liquid does not resist (as the sand, which is incompressible under the compression and does not resist under “tension;” cf. the appendix to the book [16]).

Once there is no attraction, there is no negative pressure ‘under the “tension”, i.e., there is no formation of holes. If $\gamma < 0$, then the plane (Z, P) is positive again, and therefore it is covered by the other sheet. It can readily be seen that the lines entering the point $Z = 0$, $P = 0$ (i.e., to the point $\gamma = 0$) are reflected on this second sheet back, along the same line. This means that it is geometrically convenient to arrange the reflection of vectors on the second sheet by using the matrix $-I$, where I stands for the two-dimensional identity matrix, i.e., to flip (carry out the mirror reflection for) the sheet $\gamma < 0$ to the negative quadrant.

Note that this procedure is compliance with the concepts of Dirac hole theory, just in the opposite direction, namely, to a hole we assign a negative pressure, i.e., a negative energy. Now the straight lines can be continued through the origin to the negative quadrant, although the pressure really does not change its sign. This is only a convenient geometric “uniformization.”

Note also that, due to absence of attraction, an ideal liquid is completely plastic; namely, it does not try to return to the original state (the state before stretching). In this sense, the Bose condensate for $\gamma < 0$, which leads to this “kind” of liquid, can also be treated more visually as a

glass or an amorphous solid³. This makes it possible to interpret the state of the liquid for $\gamma < 0$ more intuitively.

Remark 3. The author has come to the revision of the thermodynamics when studying economics in which money is the very particles, according the correspondence principle derived by Irving Fisher. Fisher himself did not referred to his observation as the correspondence principle. However, since he was a disciple of Gibbs, there is a clear reason for the fact that the relation of the basic law of economics

$$PQ = Mv, \quad (27)$$

where Q stands for the amount of goods, M for the number of money, v for the turnover rate, and P for the price of goods, is obviously related to the correspondence of economical and thermodynamical quantities, namely, the volume V corresponds to the amount of goods Q , the number of money M to the number of particles N , the rate v to the temperature T . The price of goods P is related to pressure to a lesser extent; however, it is denoted by the same symbol.

In this correspondence principle, it is natural to correspond holes to debts and acquitting to annihilation.

As mentioned above, the locus on which the chemical potential is zero gives the points of maximum entropy. We refer to these points as the “new spinodal.” In economics, this new spinodal means a kind of limit for debts [15, 17].

Thus, according to the relations thus obtained, we face a double covering of the plane $\{Z, P\}$ for $\gamma \geq 0$ and $-1 \leq \gamma < 0$. The meaning of the second sheet is that, for $-1 \leq \gamma < 0$, the chaotic state of liquid (as a phenomenon associated with the Bose condensate) increases when the number of holes of the type of Frenkel excitons increases, and the holes are placed in the liquid, which is fluctuationally concentrated on a rather slow-moving domain (*from the point of view of the device discussed above*⁴), in the form of chaotic nanoholes, then the structure of the liquid becomes chaotically stretched.

Here the holes-excitons cannot be indexed by our device, as well as the particles, and we can speak only of the density of holes. As was already said above, it is more convenient to place the second sheet under consideration in the quadrant $[-Z, -P]$, by continuing the straight lines (19) through the singular point of $Z = 0$, $P = 0$ to the negative quadrant. In other words, to make a reflection with the help of the matrix $-E$, where E stands for the identity matrix.

Thus, it becomes convenient to speak of “negative pressure”, although we neglect the attraction of particles, and hence there can be no negative pressure at all. As a rule, the pressure, as well as the temperature, is regarded as a positive quantity. We stretch the liquid, and it becomes plastically frozen up in this stretched state and does not tend to shrink back.

Let us explain from the point of view of physics why the extension to the negative square is natural. We compare the new ideal gas with sand, which is incompressible under the “compression” and “dost not resist” under stretching, because there is no attraction between the grains.

Example 4. Consider a cylindrical vessel, filled with sand, whose lid is attached to the piston, in the room of the space station. The increase in the vessel with the piston leads only to a rearrangement of sand and its transformation to a floating “dust” in the new volume (see [18]).

If we take into account the gravitational attraction between the grains, then the phenomenon of pulling the piston creates a negative pressure, and thus it is natural to pass to the negative quadrant on the (P, Z) diagram, and then to neglect the gravitational attraction.

Neglecting the presence of attraction here is just as “legitimate” as it is in the theory of vapor-liquid equilibrium, where the condition that the pressures are equal is possible only if we neglect the surface tension.

This also explains a smooth transition (without a phase discontinuity of the first kind) of this structure into ice, namely, a frozen glass crystallizes.

³Physicists know that glass is a liquid and an amorphous metal is a glass. Hence, an amorphous metal is a liquid. It is probable that the reader will interpret excitons (holes in amorphous metals) in a simpler way than holes in liquids because the notion of holes in crystal metals is rather customary.

⁴In reality, the holes can change places with each other and with holes in the surrounding gas quickly and imperceptibly for the eyes and for the device.

2.5. Critical exponents as observable quantities under the Wiener quantization and the derivation of the Maxwell rule

Mishchenko and the author [19] considered the transition to a two-dimensional Lagrangian manifold in the four-dimensional phase space, where the pressure P and the temperature T (the intensive variables) play the role of coordinates and the extensive variables (the volume V and the entropy S) play the role of momenta for the Lagrangian manifold, where the entropy is the action generating the Lagrangian structure.

Seemingly, there is no global canonical transformation leading to a change of this kind. This does not confuse physicists. For example, in §25 of [2], “Equilibrium of a solid in an external field,” it is said that “from the equation

$$dE = T ds + \mu dN, \quad (28)$$

represented in the form

$$dS = \frac{dE}{T} - \frac{\mu}{T} dN, \quad (29)$$

we see . . . ”

However, formula (28) *does not imply* the expression “represented in the form” (29). Nevertheless, this “implies” the following conclusion: “If the field is absent and both μ and T are constant, then the pressure is automatically also constant.” At the same time, the same textbook states that, at a temperature slightly below the “dew point,” “when the radius of the drop becomes greater than the critical value, it can be seen that the pressure of the liquid inside the drop differs from the pressure in the saturated vapor. The external field is absent. Is this still thermodynamics? Other words are used; one speaks of a vapor instead of gas and of the process of nucleation instead of the vapor-liquid equilibrium. And then a patch is immediately put on the same hole, namely, an extra term is added to (29). The old thermodynamics has many patches of this kind.

It turns out that this complex transformation, leading to relation (29), can be carried out, as we have seen, only by continuing to the domain of negative energies. After this, one can justify the Maxwell transition by introducing a small dissipation (viscosity). The introduction of an infinitesimal dissipation enables one to simultaneously solve the problem of critical exponents, without using the scaling hypothesis, on which the method of renormalization group is based. Let us show this.

In thermodynamics, the viscosity is absent. However, generally speaking, without an infinitesimal dissipation, an equilibrium in thermodynamics should not be attained. Therefore, it is natural to implement the occurrence of this infinitesimal viscosity and then pass to the limit as the viscosity tends to zero.

The geometric quantization of the Lagrangian manifold (see [20], §11.4) is usually associated with the introduction of the constant \hbar . The author introduced the term of Wiener (or tunnel) quantization to describe the case in which the number \hbar is purely imaginary [21, 22].

Let us apply the Wiener quantization to thermodynamics. The thermodynamic potential $G = \mu N$ is the action $S = \int p dq$ on the two-dimensional Lagrangian manifold Λ^2 in the four-dimensional phase space q_1, q_2, p_1, p_2 , where q_1 and q_2 are the pressure P and the temperature T , respectively, p_1 is equal to the volume V , and p_2 is equal to the entropy of S taken with the opposite sign. All other potentials, namely, the internal energy E , the free energy F , and the enthalpy W are the results of projecting the Lagrangian manifold to the coordinate planes p_1, p_2 ,

$$E = - \int \vec{q} d\vec{p}, \quad \vec{q} = \{q_1, q_2\}, \quad \vec{p} = \{p_1, p_2\}, \quad W = - \int (q_2 dp_2 + q_1 dp_1), \quad F = \int (q_1 dp_1 - q_2 dp_2). \quad (30)$$

Under the Wiener quantization, we have

$$N = \varepsilon \frac{\partial}{\partial \mu}, \quad V = \varepsilon \frac{\partial}{\partial p}, \quad S = -\varepsilon \frac{\partial}{\partial T}.$$

Consequently, the role of time t in the quantization, is played by $\log(\mu/T)$,

$$G = \mu N \sim \varepsilon \frac{\mu}{T} \frac{\partial}{\partial (\mu/T)} = \varepsilon \frac{\partial}{\partial \log(\mu/T)}.$$

Note that the tunnel quantization of the van der Waals equation (vdW) as $\varepsilon \rightarrow 0$ gives Maxwell's rule (see below).

As we shall see below, the critical point and the spinodal point are focal points, and therefore, as $\varepsilon \rightarrow 0$ these points do not come to the "classical" picture, i.e., to the van der Waals model. The spinodal points, which are similar to turning points in quantum mechanics, can be approached by the Airy function, whereas the critical point, which is the point at which two turning points are generated (two Airy functions), can be approached by the Weber function (see [23]). It is the very Weber function which is used to express the creation point of the shock wave for $\varepsilon \rightarrow 0$ in the Burgers equation is expressed. If one passes to the limit as $\varepsilon \rightarrow 0$ outside these points, then we obtain the vdW–Maxwell model. However, the passage to the limit is violated at these very points. Therefore, the so-called Landau "classic" critical exponents [2] drastically differ from the experiment. The Weber function give singularities of the form $\varepsilon^{-1/4}$, whereas the Airy function gives a feature of the form $\varepsilon^{-1/6}$.

Let us present a more detailed consideration of the Burgers equation.

Consider the heat equation

$$\frac{\partial u}{\partial t} = \frac{\varepsilon}{2} \frac{\partial^2 u}{\partial x^2}, \quad x \in \mathbb{R}, \quad t \geq 0, \quad (31)$$

where $\varepsilon > 0$ is a small parameter. As is known, all linear combinations

$$u = \lambda_1 u_1 + \lambda_2 u_2 \quad (32)$$

of solutions u_1 and u_2 of equation (31) are solutions of this equation.

Let us make the change

$$u = \exp(-w(x, t)/\varepsilon). \quad (33)$$

We obtain the following nonlinear equation:

$$\frac{\partial w}{\partial t} + \frac{1}{2} \left(\frac{\partial w}{\partial x} \right)^2 - \frac{\varepsilon}{2} \frac{\partial^2 w}{\partial x^2} = 0, \quad (34)$$

which is referred to as the integrated Burgers equation⁵. Obviously, to any solution u_i of equation (31) we can assign a solution $w_i = -\varepsilon \log u_i$ of the equation (34), $i = 1, 2$. To the solution (32) of equation (31) we assign a solution

$$w = -\varepsilon \log \left(e^{-\frac{w_1 + \mu_1}{\varepsilon}} + e^{-\frac{w_2 + \mu_2}{\varepsilon}} \right)$$

of the equation (34) where $\mu_i = -\varepsilon \log \lambda_i$, ($i = 1, 2$). Since

$$\lim_{\varepsilon \rightarrow 0} w = \min(w_1, w_2),$$

we obtain the (min, +) algebra of the tropical mathematics [24].

To find solutions for $t > t_{\text{cr}}$, Hopf suggested to consider the Burgers equation

$$\frac{\partial v}{\partial t} + v \frac{\partial v}{\partial x} - \frac{\varepsilon}{2} \frac{\partial^2 v}{\partial x^2} = 0, \quad v|_{t=0} = p_0(x), \quad (35)$$

and to refer to the function $p_{\text{gen}} = \lim_{\varepsilon \rightarrow 0} v$ (Riemann waves) as a (generalized) solution of the equation

$$\frac{\partial p}{\partial t} + p \frac{\partial p}{\partial x} = 0, \quad p|_{t=0} = p_0(x). \quad (36)$$

⁵The usual Burgers equation can be derived from equation (34) by differentiating with respect to x and by using the substitution $v = \partial w / \partial x$.

The solution v of the Burgers equation can be expressed in terms of the logarithmic derivative

$$v = -\varepsilon \frac{\partial}{\partial x} \log u \quad (37)$$

of the solution u of the heat equation

$$\frac{\partial u}{\partial t} = \frac{\varepsilon}{2} \frac{\partial^2 u}{\partial x^2}, \quad u|_{t=0} = \exp \left\{ -\frac{1}{\varepsilon} \int_{-\infty}^x p_0(x) dx \right\}. \quad (38)$$

Thus, the original problem reduces to the study of the logarithmic limit of a solution of the heat equation. As is known, the solution of problem (38) is of the form

$$u = (2\pi\varepsilon t)^{-1/2} \int_{-\infty}^{\infty} \exp \left\{ -\left((x-\xi)^2 + 2t \int_{-\infty}^{\xi} p_0(\xi) d\xi \right) / 2th \right\} d\xi. \quad (39)$$

The asymptotics of the integral (39) can be calculated by the Laplace method. For $t < t_{\text{cr}}$, we have

$$u = (|J|^{-1/2}(\xi(x, t), t) + O(\varepsilon)) \exp \left\{ -\frac{1}{\varepsilon} \mathcal{S}(x, t) \right\}. \quad (40)$$

Here

$$\mathcal{S}(x, t) = \int_{-\infty}^{r(t)} p dx,$$

and the integral is evaluated along a Lagrangian curve Λ^t ; $r(x)$ is a point on Λ^t . For $t > t_{\text{cr}}$, there are three points $r_1(x)$, $r_2(x)$, and $r_3(x)$ on Λ^t whose projections to the x axis are the same; in other words, the equation $Q(t, \xi) = x$ for $x \in (x_1, x_2)$ has three solutions $\xi_1(x, t)$, $\xi_2(x, t)$, and $\xi_3(x, t)$.

Write

$$\tilde{\mathcal{S}}(x, t) = \int_{-\infty}^{r(x)} p dx \quad \text{for } x < x_1, \quad x > x_2,$$

$\tilde{\mathcal{S}}(x, t) = \min(\mathcal{S}_1, \mathcal{S}_2, \mathcal{S}_3)$, and

$$\mathcal{S}_j = \int_{-\infty}^{r_j(x)} p dx,$$

where $J \in \{1, 2, 3\}$ for $x \in [x_1, x_2]$.

These arguments enable us to obtain a generalized discontinuous solution of (36) for the times $t > t_{\text{cr}}$. It is defined by a function $p = p(x, t)$ defining the significant areas [21] of the curve Λ^t . Note that this, in particular, implies the rule of equal areas, which is known in hydrodynamics for finding the front of a shock wave whose evolution is described by equation (36). Note that this precisely corresponds to the Maxwell rule for the vdW equation.

The solution $v = v(x, \varepsilon)$ of the Burgers equation at the critical point $x = p^3$ is evaluated by the formula

$$v(x, \varepsilon) = \varepsilon \frac{\partial \log u(x)}{\partial x} = \frac{\int_0^{\infty} \exp\left\{\frac{-x\xi - \xi^4/4}{\varepsilon}\right\} \xi d\xi}{\int_0^{\infty} \exp\left\{\frac{-x\xi - \xi^4/4}{\varepsilon}\right\} d\xi}. \quad (41)$$

As $x \rightarrow 0$, after the change $\frac{\xi}{\sqrt[4]{\varepsilon}} = \eta$, we obtain

$$v(\varepsilon, x) \rightarrow_{x \rightarrow 0} \sqrt[4]{\varepsilon} \cdot \text{const}. \quad (42)$$

What does this mean in terms of classical theory and classical measurement, when the condition referred to in the book [1] as the “semiclassic condition” is satisfied (i.e., for the case in which

we are outside the focal point)? For the Laplace transform, this means that we are in a domain in which the Laplace asymptotic method can be applied indeed, i.e., in the domain where

$$u(x) = \frac{1}{\sqrt{\varepsilon}} \int_0^\infty e^{-\frac{px - \tilde{S}(p)}{\varepsilon}} dp. \tag{43}$$

If the solution of the relation

$$x = \frac{\partial \tilde{S}}{\partial p} \tag{44}$$

is nondegenerate, i.e., $\frac{\partial^2 \tilde{S}}{\partial p^2} \neq 0$ at the point at which $\frac{\partial \tilde{S}}{\partial p} = x$, then the reduced integral (43) is bounded as $\varepsilon \rightarrow 0$. For this integral to have a zero of the order of $\varepsilon^{1/4}$, we must integrate it with respect to x after applying the fractional derivative $D^{-1/4}$. The value of $D^{-1/4}$ as applied to 1 (the value of $D^{-1/4}1$ is approximately equal to $x^{1/4}$).

By the uncertainty principle, [25], the correspondence between the differentiation operator and a small parameter of the form $D \rightarrow 1/\varepsilon$ is preserved for the ratio $-\varepsilon \frac{\partial u / \partial x}{u}$, while the leading term of the asymptotic behavior is not cancelled in the difference between $\frac{\partial^2 u / \partial x^2}{u}$ and $\frac{(\partial u / \partial x)^2}{u^2}$ due to the uncertainty principle (see Remark 4).

Remark 4. Let us repeat the calculations in [1] with regard to the fact that, on this class of functions, \overline{D} has the properties $\int \varphi D \varphi dx = \frac{1}{2} \int D \varphi^2 dx = 0$ and $\int x \varphi^2 dx = 0$.

Consider the obvious inequality

$$\int_{-\infty}^{+\infty} \left| ax\psi + \frac{d\psi}{dx} \right|^2 dx \geq 0, \tag{45}$$

where a is an arbitrary real constant. When evaluating this integral, we have

$$\begin{aligned} \int x^2 |\psi|^2 dx &= \overline{(\Delta x)^2}, \\ \int \left(x \frac{d\psi^*}{dx} \psi + x \psi^* \frac{d\psi}{dx} \right) dx &= \int x \frac{d|\psi|^2}{dx} dx = - \int |\psi|^2 dx = -1, \\ \int \frac{d\psi^*}{dx} \frac{d\psi}{dx} dx &= - \int \psi^* \frac{d^2 \psi}{dx^2} dx = \frac{1}{\varepsilon^2} \int \psi^* |D|^2 \psi dx = \frac{1}{\varepsilon^2} \overline{|\Delta D|^2}. \end{aligned} \tag{46}$$

We obtain

$$a^2 \overline{(\Delta x)^2} - a + \frac{1}{\varepsilon^2} \overline{|\Delta D|^2} \geq 0. \tag{47}$$

For this quadratic trinomial (in a) to be positive for all values of a , it is necessary that the following condition be satisfied:

$$4 \overline{(\Delta x)^2} \frac{1}{\varepsilon^2} \overline{|\Delta D|^2} \geq 1$$

or

$$\sqrt{\overline{(\Delta x)^2} \overline{|\Delta D|^2}} \geq \frac{\varepsilon}{2}. \tag{48}$$

Thus, the tunnel quantization explains both the condition $\mu = 0$ for photons and the condition $\mu \leq 0$ for bosons.

In the case of thermodynamics, the role of x is played by the pressure P , and the role of the momentum p is the played by the volume V . Therefore, $V \sim P^{1/4}$, i.e.,

$$P_c \sim (V - V_c)^4. \tag{49}$$

This is the very jump of the critical exponent. One can similarly obtain other critical exponents (see [25]). For the comparison with experimental data, see the same paper.

Unfortunately, thermodynamics does not use the concept of Lagrangian manifold which was introduced by the author in 1965 [26]. It is especially suitable for thermodynamics, in which there are pairs of intensive and extensive quantities. Intensive quantities, roughly speaking, are the quantities for which one cannot create the concept of “specific” quantity. These are the temperature T , the pressure P , and the chemical potential μ . To these intensive quantities, there correspond related extensive quantities, namely, the entropy S , the volume V , and the number of particles N . Altogether, they form the phase space, where the role of coordinates is played by the intensive quantities and the role of momenta is played by the extensive quantities. In this case, a Lagrangian manifold is a three-dimensional submanifold (of the six-dimensional phase space) on which there is an action, an analog of the integral $\mathcal{S} = \int p dq$, $q \in \mathbb{R}^2$, $p \in \mathbb{R}^2$ in mechanics. It is locally independent of the path.

Usually a 4-dimensional phase space $T, S; P, V$ is considered. This space corresponds to $q \in \mathbb{R}^2$, $p \in \mathbb{R}^2$, $q_1 \rightarrow T$, $q_2 \rightarrow P$, $p_1 \rightarrow S$, $p_2 \rightarrow V$: $d\mathcal{S} = p_1 dq_1 + p_2 dq_2$, depending on the coordinate plane of the form q_1, q_2 ; q_1, p_2 ; p_1, q_2 ; p_1, p_2 , to which the Lagrangian manifold is projected.

The Lagrange property means that the number of planes cannot coincide (there are no planes of the form q_1, p_1 and q_2, p_2). To every projection there corresponds some potential (q_1, q_2 is the thermodynamic potential, etc.).

This is an obvious correspondence. If it were more elaborated, then, on one hand, the transition from the action $d\mathcal{S} = p_1 dq_1 + p_2 dq_2$ to the “action”–coordinate $dq_1 = d\mathcal{S}/p_1 - (p_2/p_1) dq_2$ would be not “so obvious” (see formulas (28)–(29)). On the other hand, it would be natural to use the semiclassical (Wiener) quantization of action rather than the scaling hypothesis.

(The quantization of the Lagrangian manifold differs from the full quantization of thermodynamics [27] in the same way in which the semiclassical Bose–Sommerfeld geometric quantization differs from the quantization of Schrödinger, Heisenberg, and Feynman.)

The term “dequantization,” which is well-known in the tropical mathematics [24], means the Wiener or tunnel quantization of the Lagrangian manifold, and then the passage to the limit as the quantization parameter (the viscosity) tends to zero.

3. CONSIDERING THE ATTRACTION. DIMERS (PAIRS) AS OBSERVABLE QUANTITIES

3.1. Second quantization of classical mechanics and ultrasecond quantization of thermodynamics. Operators of creation and annihilation for pairs-dimers

The second quantization is always associated with the identity of particles, and, if it is carried out for classical particles, then it is tacitly assumed that the particles are indistinguishable for the observer. Instead of an N -dimensional problem, we arrive at the three-dimensional picture in which N particles are distributed. The Vlasov equation [28, 29] is obtained from the second quantization of classical mechanics. However, the original arguments used by Vlasov were actually based on the assumption that the particles can be regarded as identical ones.

In the classical system of Hamilton equations for N particles, even if the Hamiltonian is invariant under any permutation of the particles, the initial conditions need not have this property. However, the initial conditions of the Liouville equation can be regarded as data satisfying the conditions of symmetry.

Indeed, let

$$\{q_i^0, p_i^0\}, \quad (q_i^0 = q_{i,1}^0, q_{i,2}^0, q_{i,3}^0, \quad p_i^0 = p_{i,1}^0, p_{i,2}^0, p_{i,3}^0) \quad (50)$$

are initial conditions for the Hamiltonian system whose Hamiltonian is invariant under every permutation p_i, p_j and also under every permutation q_i, q_j . For example, let

$$H(p, q) = \sum \frac{p_i^2}{2m} + \sum \sum V(|q_i - q_j|). \quad (51)$$

Substituting the initial conditions into the Hamiltonian (51), we obtain the energy

$$E = H(p^0, q^0). \quad (52)$$

The energy is conserved along the trajectories of the Hamiltonian system.

Consider further the Liouville equation corresponding to the Hamiltonian system

$$\frac{\partial \rho}{\partial t} = \{H(p, q), \rho\}, \quad (53)$$

where $\{\cdot\}$ stands for the Poisson bracket, with the initial condition

$$\rho(E), \quad \rho(E) \in C^\infty,$$

where E satisfies (52). This equation describes the distribution corresponding to the Hamiltonian system with the initial conditions given above.

The Liouville equation and the initial conditions are symmetric with respect to any transposition of p_i and p_j and to any transposition of q_i and q_j . This symmetry is preserved for the solutions. According to the Gibbs distribution for the Gibbs Ensemble, every distribution can be expressed in terms of energy. Therefore, it is symmetric with respect to any permutation of the particles.

Schönberg [30] carried out a second quantization of this system in the Fock space⁶. In [29], the Vlasov equation was obtained under the assumption that the interaction is small and the number of particles is large. The BBKKI chains are also symmetric with respect to these permutations. Hence, for any distribution in the many-body problem, such a symmetry follows. Thus, we arrive at the invariance with respect to the permutations of the particles, and thus to a “distribution of Bose–Einstein type” for the statistical physics of classical particles. Other mathematically rigorous arguments which lead to a “distribution of Bose–Einstein type,” in the form of lemmas and theorems (see [31]), and hence also the distributions of classical particles, obey the laws of number theory.

Although a modern macroinstrument cannot trace the motion of every particle, which is possible at the classical level, but it can distinguish between molecules and dimers or clusters. The clusters consisting of more than two molecules occur in gas much less frequently than dimers. Dimers are observable at all temperatures, and a macroinstrument can calculate their average percentage at a given temperature. This is an important new phenomenon in experiment, and this phenomenon was not available to the great who formulated the basic laws of thermodynamics.

Dimers occur and become immediately split by monomers (single molecules), and they are created and annihilated in different places. They occur because there are *quantum* forces of attraction between molecules (the dipole-dipole interaction). The dimers are virtual, as the ideal liquid is.

To take into account this important phenomenon (the creation and annihilation of dimers) mathematically, one obviously needs to make the “second” quantization and introduce the creation and annihilation operators for dimers, i.e., for pairs. The author referred to this “second” quantization as the “ultrasecond” quantization due to the introduction of creation and annihilation operators for pairs. In the special case of the Bardeen model, this quantization was introduced in essence [32], [29]; however, since this model is, roughly speaking, exactly solvable, these operators turned out to be hidden in the model in a sense.

In general, the ultrasecond quantization and the asymptotic behaviors associated with it are rather cumbersome and lead to quantum equations involving the Planck constant \hbar . The passage to the limit as $\hbar \rightarrow 0$, and then the passage to the limit as the viscosity tends to zero, are cumbersome, and we present here only a part of this passage, which is related, as in the previous section, with the introduction of an infinitesimal viscosity into the classical scattering problem (for $\hbar = 0$). This means that we introduce the viscosity and, after manipulations, pass to the limit as the viscosity tends to zero. This procedure will enable us to find the Boyle temperature T_B , and then also the Boyle density ρ_B , i.e., the so-called Zeno line, which is present in the van der Waals model and which was first noticed by Bachinski in experiments with pure gases.

We shall further obtain the so-called law of corresponding states.

3.2 Boyle temperature as the temperature above which the dimers are not observable in the Boltzmann–Maxwell ideal gas

The attraction between the particles occurs in the quantum mechanical consideration of the dipole-dipole interaction. In the standard semiclassical limit, if the distance between neutral molecules is fixed (does not depend on the parameter \hbar , i.e., on a dimensionless parameter proportional

⁶This space exists only under the assumption that the particles are indistinguishable (the “commutativity,” or the invariance).

to \hbar), then, as $\hbar \rightarrow 0$, the attraction disappears. In this sense, the use of an attraction potential in molecular dynamics using the classical Newton equations for many particles is at least baseless.

However, if, along with \hbar , the problem involves other small and large parameters, then the attraction potential can be kept for some relationships among these parameters under the passage to the limit as $\hbar \rightarrow 0$.

Since the scattering problem has another parameter tending to infinity, for example, the time of scattering is considered in the interval from $-\infty$ to $+\infty$, it can happen that, as $\hbar \rightarrow 0$ and $t \rightarrow \infty$ simultaneously (provided that there is a dependence between these parameters), an attractive potential of the order of r^{-6} is kept (as $\hbar \rightarrow 0$), where r stands for the distance between the particles. As an example, we consider the Lennard–Jones potential, noting that, in our fundamental manipulations, the repulsive part of the potential does not play any role.

The only essential quantity is the so-called effective radius a , because it determines a one-dimensional elementary length.

As is known, in the radially symmetric case,

$$\frac{mv^2}{2} + \frac{M^2}{2mr^2} + \Phi(r) = E. \quad (54)$$

In the original scattered particles, we prescribe an energy E and an impact parameter B . The momentum M , as well as the energy E , is preserved. We also know that

$$M^2 = B^2 E. \quad (55)$$

Expressing the energy E , we obtain for the attraction

$$E = \frac{(mv^2)/2 + \Phi(r)}{1 - B^2/r^2} \quad (56)$$

in the domain $r \leq B$.

In the scattering problem, for the interaction potential, one considers the Lennard–Jones potential

$$\Phi(r', r'') = 4\varepsilon \left(\frac{a^{12}}{\|r' - r''\|^{12}} - \frac{a^6}{\|r' - r''\|^6} \right), \quad r = r' - r'', \quad (57)$$

where ε stands for the energy at the well depth, a for the effective radius, and $\|r' - r''\|$ for the distance between two particles with radius vectors r' and r'' . In the two-particle problem, in the absence of external potential, the problem is reduced to a one-dimensional radially symmetric problem.

In problem (56), for different values of B , there are other barriers and wells. At the stationary points E_{\min} and E_{\max} , the velocity vanishes, and thus these values can be evaluated by using the potential term only.

We speak now of a pair of particles with the mass center which is caught by the trap (rather than of a single particle). Therefore, the difference $E_{\max} - E_{\min}$ is the very energy which is needed to knock out the pair (dimer) from the trap.

In an experiment, the percentage of dimers in gas can be calculated. It can be seen how dimers are created and how they are annihilated (broken by monomers). After this, the average number of these events is calculated. The higher is the temperature, the higher is the average energy of the monomers, and the smaller is the number of dimers.

The main point is that, under this approach, there are only two values, E_{\max} and E_{\min} , which are kept in the skeleton of the scattering problem (cf. the skeleton of the amoeba in the tropical mathematics [24]). For $E_{\max} = E_{\min}$, the well disappears. For the attractive part of the Lennard–Jones potential, this energy is equal to 0.8ε . With regard to the standard Clausius considerations⁷,

⁷Following Clausius, experts in molecular physics usually argue by proceeding from the symmetry of the motion of a molecule averaged in all six directions. In the scattering problem, we use the principle of symmetry in all directions, which is standard in molecular physics, but apply it to define specific quantities of molecular physics rather than the mean free path. Therefore, the fraction of all particles that moves head-on is $1/12$. There are three such directions; hence, one quarter of all molecules collide. The arguments concerning symmetry that were used by Clausius to evaluate the free path length (and are repeated here by the author) are quite approximate. However, these arguments do not modify the values of the ratios of the form T_B/T_C . This very ratio is of interest for us.

we can see that the average energy of the particles is equal to $\frac{16}{5}\varepsilon$. The average energy is the temperature, and $T = \frac{16}{5}\frac{\varepsilon}{k}$. Above this temperature, there is no well. In thermodynamics, for physical reasons, this is the so-called Boyle temperature T_B . In our framework, the Boyle temperature is defined as the temperature above which the dimers are practically absent. This is a new approach. According to this conception, the Boyle temperature for argon (Ar) is $T_B = 382\text{ K}$ and for krypton (Kr) it is $T_B = 547\text{ K}$, while the tables of the experimental work [33] give $T_B = 392\text{ K}$ for Ar and $T_B = 538\text{ K}$ for Kr. The discrepancy between the theoretical and experimental values is of the order of 2–3%.

The critical temperature E_{\max} must correspond to the deepest well, i.e., to the maximum value of the difference $E_{\max} - E_{\min}$ for all impact parameters B . This difference determines the drop of the energy of a dimer after this dimer was captured by the “trap,” and thus determines the energy which a monomer must have to knock out the dimer from the well (i.e., for the dimer to collapse).

The height of the barrier “protects” the created pair whose reduced mass was captured by the trap of “dimers” and “clusters” from “shocks” of monomers. As the temperature decreases, $T < T_c$, the height of the barrier reduces, and, to survive, the clusters must create their own barrier in the form of a microanalog of the surface film. Thus, a “domain” must occur, a three-dimensional cluster (the so-called elementary cluster) which has at least one particle which is protected by other particles.

This is a new definition of the critical temperature T_c as the temperature below which clusters are formed from dimers. Calculations give $E_{\max} = 0.286\frac{\varepsilon}{k}$ at the point $\max_B(E_{\max} - E_{\min})$. The impact parameter at this point is equal to $B = 2.436$. The only dimensionless quantity in our problem (which is evaporated to the skeleton) is the quantity $\frac{E_{\min}}{E_{\max}}$. In other words, we have kept only the skeleton of the problem, namely, two stationary points.

Since $\frac{E_{\min}}{E_{\max}}$ is a dimensionless quantity, and we relate E_{\max} (as the average energy) to the temperature (multiplied by the density ρ), it follows that the above ratio coincides with the compressibility factor $Z = \frac{PV}{RT} = \frac{E_{\min}}{E_{\max}}$.

3.3 Macroinstruments and microinstruments in dimension theory. determinin the maximum density ρ_B and the Zeno line which borders the domain of dimers as the density is modified

Let us now obtain analytical formulas for the Zeno line in dependence on the potential.

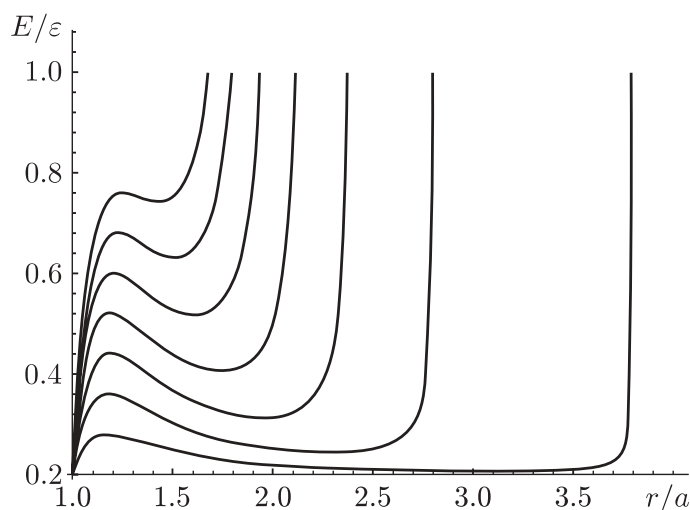


Fig. 6. Wells and barriers in the scattering of two particles with the Lennard–Jones interaction potential at different impact parameters B .

Let us use considerations of dimensional analysis for the scattering problem and the definition of the one-particle (the so-called thermal) attraction potential. The scattering problem is considered for the Lennard–Jones potential, and therefore there is an additional parameter of length in the

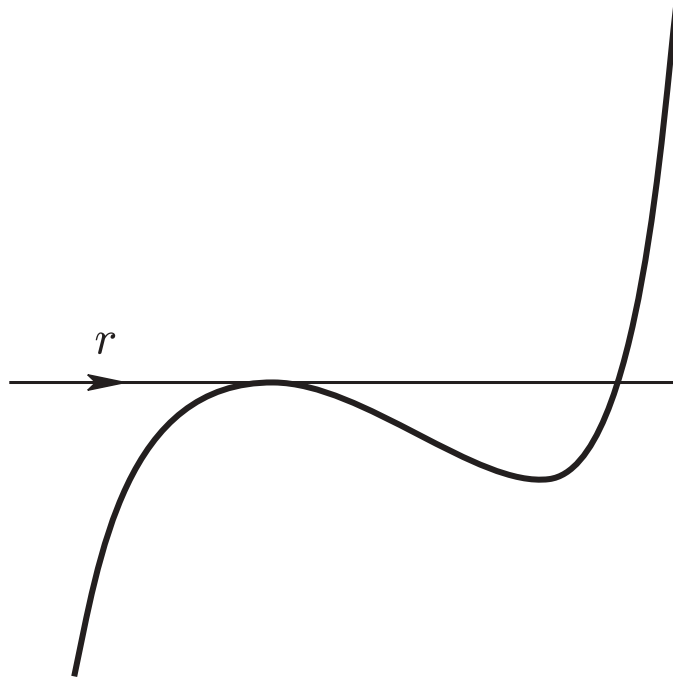


Fig. 7. A trap for a fictitious particle–dimer, in the center of mass system (CMS). Here r stands for the radius vector of the dimer; it is marked on the abscissa axis. A “particle” falls from the left, from the point $r = B$, where B stands for the impact parameter.

problem, the parameter a , which is the effective radius. The attraction potential occurs in the quantum theory of the dipole–dipole interaction. If we fix the distance between the particles and assume that the semiclassical parameter \hbar tends to zero, then the attractive potential vanishes. This means that, as $\hbar \rightarrow 0$, the distance between the particles decreases. It follows that

- 1) it is at least incorrect to use an attractive potential in a problem of molecular dynamics for a classical system of Newton’s equations;
- 2) the attractive potential acts between “nearest neighbors” only.

Therefore, it is natural to use the expansion of an attraction single-particle potential in powers of the radius r up to $O(r^3/V)$ only.

The “dressed” or thermal potential $\Psi(r^2)$ is attracting. As is well known, it was derived from the fact that the correlation sphere for the N -particle for the Gibbs distribution is finite [34].

One of the most interesting points of independence of a macroinstrument of a microinstrument manifests itself when applying the dimension theory [35]. A macroinstrument determines the volume V . According to the independence of the thermodynamic quantities on the shape of the volume V , the volume V ensures us that we have the dimension in the dimension theory is three; however, this volume does not give us any one-dimensional measure, which is the typical length in the thermodynamic process.

A microinstrument determines the effective radius of the molecule and the mean free path. However, in dimension theory, we cannot measure the typical length of the macrothermodynamics by using the radius of the molecule or the mean free path, even if the volume is a Torricelli tube and its typical thickness is small as compared with the case in which the vessel is a ball. These considerations show that the only possible dimensionless combination for the argument of $\Psi(r^2)$ is

$$\Psi\left(\frac{ar^2}{V}\right).$$

Since $a^3 \ll V$, it follows that the expansion is

$$\Psi\left(\frac{ar^2}{V}\right) = C_1 + C_2 \frac{ar^2}{V} + O\left(\frac{a^2 r^4}{V^2}\right). \quad (58)$$

The constant C_1 gives no contribution to the scattering problem, and the thermal “single-particle” potential turns out to be proportional to the density. On the plane $\{T, \rho\}$, the maximum of the binodal (according to Fig. 8 for $T = T_c$) is equal with respect to ρ to the very value ρ_c , which enables us to find the proportionality coefficient. It turns out to be equal to one.

The situation in which the thickness of the tube is “commensurable” to the radius of the molecule⁸ leads to quite different effects: to the superfluidity of water in a nanotube and to the freezing of water at $T^0 = 5K$ (see [36]).

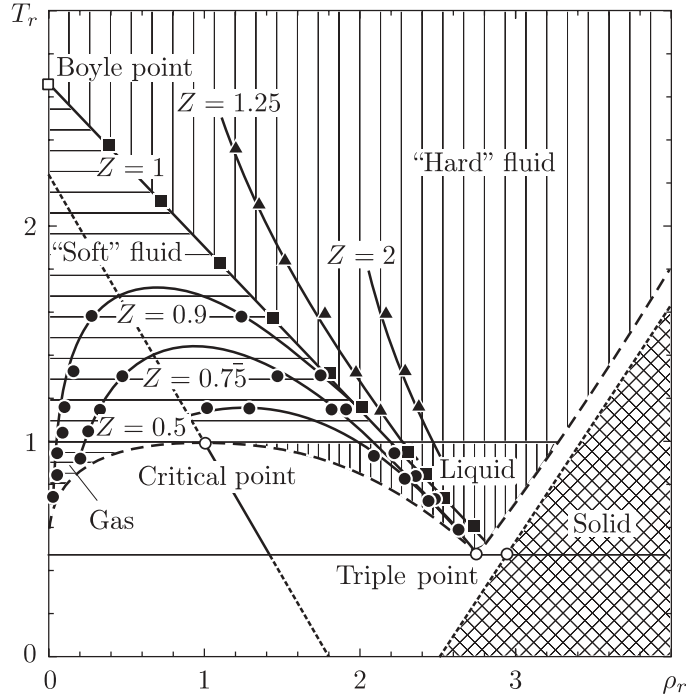


Fig. 8. The T - ρ -diagram for gases corresponding to simple liquids. Here $T_r = T/T_c$ and $\rho_r = \rho/\rho_c$. The Zeno line (the straight line $Z = \frac{PV}{kNT} = 1.0$) in the phase diagram. For the states $Z > 1.0$ (the hard fluids), the repulsive forces dominate; for the states $Z < 1.0$ (soft fluids), the attraction forces dominate.

Expanding

$$r^2 = r_1^2 + r_2^2 = \frac{(r_1 - r_2)^2}{2} + \frac{(r_1 + r_2)^2}{2}, \tag{59}$$

we can make the separation of variables in the two-particle problem to a scattering problem for a pair of particles and to the problem of their joint motion for $r_1 + r_2$, just as it was done in [37]. In this case, in the scattering problem, a quadratic attraction potential (an upturned parabola) $-\rho r^2$ is added to the Lennard–Jones interaction potential, and $\rho = \frac{1}{V}$ for the isochoric process.

In the scattering problem thus obtained, there are two points of rest, namely, the stable one, E_{\min} , and the unstable point E_{\max} . Their ratio is a dimensionless quantity. As follows from the previous section, $Z = \frac{PV}{NT}$, where P stands for the pressure, N for the number of particles, T for the temperature, and, due to the fact that a stable stationary point has the meaning of temperature, it follows that the ratio

$$Z = \frac{PV}{NT} = \frac{E_{\min}}{E_{\max}} \tag{60}$$

enables us to write the curves $Z = \text{const}$ in the graph $T, \rho = \frac{N}{V}, .$

⁸When the scales become “commensurable” in this sense, another thermodynamics arises [27, 36].

The curve at $Z = 1$ is called the *Zeno line* (or the *Bachinski parabola*), and the locus of the beginnings of the curves Z_{\max} (for $C_2 \neq 0$ and $B \rightarrow \infty$) is referred to as the *binodal*.

Thus, in our view, the Zeno line determines the temperatures for which the dimers become practically nonexistent for a given density.

Denote by ρ_c the value of ρ at the maximal point of the binodal and denote the endpoint of this curve on the ρ axis by ρ_B . In [38], this point was referred to as the hypothetical point ρ_B (the Boyle point).

Calculating the value of Z_c , we obtain $Z_c = 0.296$, which coincides with the values of Z_c for the noble gases up to thousandths. The ratio ρ_c/ρ_B also coincides with the values of this quantity for the noble gases.

Table 1 shows the data corresponding to the resulting diagram (for $B = 100$ in “molecular” values), and note the discrepancy between the basic dimensionless relations obtained by the data of molecular dynamics and the theoretical relations obtained by physicists from the chain BBKKI and the N -partial Gibbs distribution.

Table 1

Z_c	ρ_c/ρ_B	T_c/T_B
0.29	0.273	0.36
0.308	0.285	0.38
0.375	0.333	0.296

On the top line of the table, the theoretical values for Z_c , ρ_c/ρ_B , and T_c/T_B , obtained using the above theory are presented. The second line contains the values of the same quantities evaluated according to the latest data of molecular dynamics and results of theoretical physicists for the Lennard–Jones potential. The third line gives the values obtained from the van der Waals equation, which is empirical.

The value of Z_c can be computed in the experiment very accurately, and it is equal to 0.29 for noble gases, nitrogen, oxygen, and propane. The value of ρ_c/ρ_B (the ratio of the critical value of ρ critical to ρ_B , i.e., to the entire length of the segment with respect to ρ on which the Zeno-line “cuts” the abscissa axis away) evaluated in the above theory coincides with the corresponding values for water, argon, xenon, krypton, ethylene, and a number of other gases.

Let us present detailed calculations to find the Zeno-line.

Consider the potential

$$E(r) = \frac{-\alpha r^4 + r^2 U(r)}{B^2 - r^2}. \quad (61)$$

Its first derivative is equal to

$$E'(r) = \frac{r(2B^2 U(r) + r(2\alpha r(-2B^2 + r^2) + (B^2 - r^2)U'(r)))}{(B^2 - r^2)^2}, \quad (62)$$

and the second derivative is

$$E''(R) = \frac{1}{(B^2 - r^2)^3} (2(B^4 + 3B^2 r^2)U(r) + r(-2\alpha r(6B^4 - 3B^2 r^2 + r^4) + 4(B^4 - B^2 r^2)U'(r) + r^2(B^2 - r^2)^2 U''(r))). \quad (63)$$

We obtain a solution of the equation in the form

$$B = \sqrt{-\frac{-r^3 U'(r) + r^4 U''(r)}{-8U(r) + 2rU'(r) + 2r^2 U''(r)}}. \quad (64)$$

Substituting the value $B(r)$ into (61), we find $E(\alpha)$, the Zeno-line, i.e., a segment, which is straight up to 3%, $T/T_B + \rho/\rho_B = 1$, where ρ_B stands for the maximal density as $T \rightarrow 0$.

3.4. *Limit stretching of a liquid. The maximum density of holes*

We have $Z = P/\rho T$, where $\rho = \rho_B (1 - T/T_B)$ is an isotherm-isochore. Therefore,

$$Z = \frac{P_r}{\rho_B T_r (1 - T/T_B)}. \tag{65}$$

Let us express Z in terms of γ for $Z < 0$ and $\gamma < 0$ and for $\mu \sim o(1/\log N)$,

$$N = A(\gamma)T_r, \quad P = \frac{T_r^{2+\gamma}\zeta(2+\gamma)}{\zeta(2+\gamma_c)},$$

where $T_r = T/T_c$ and $P_r = P/P_c$. The value of ρ_B is defined in this very normalization.

Therefore,

$$Z = \frac{T_r^{2+\gamma}\zeta(2+\gamma)}{\zeta(2+\gamma_c)(A(\gamma)T^2)} = \frac{T_r^\gamma\zeta(2+\gamma)}{\zeta(2+\gamma_c)A(\gamma)}. \tag{66}$$

On the other hand, $N = \rho = \rho_B (1 - T/T_B) = A(\gamma)T$. Consequently, $\rho_B/T - \rho_B/T_B = A(\gamma)$ and

$$\left(\frac{1}{T}\right)^{|\gamma|} = \left(\frac{1}{\rho_B}A(\gamma) + \frac{1}{T_B}\right)^{|\gamma|}.$$

Substituting this into (66), we obtain

$$Z = \frac{\zeta(\gamma+2)}{\zeta(\gamma_c+2)} \frac{\left(\frac{1}{\rho_B}A(\gamma) + \frac{1}{T_B}\right)^{|\gamma|}}{A(\gamma)},$$

and $A(\gamma) \rightarrow \infty$ as $\gamma \rightarrow -1$.

Therefore, as $\gamma \rightarrow -1$, the value $1/T_B$ is negligible. Consequently,

$$Z|_{\gamma \rightarrow -1} \simeq \frac{\zeta(\gamma+2)}{\rho_B^{|\gamma|}\zeta(\gamma_c+2)A(\gamma)^{1-|\gamma|}}. \tag{67}$$

Here γ_c corresponds to Z_c , which is the minimal value of Z on the critical isotherm for $P = 1$ (see Fig. 9).

Since

$$A(\gamma, \Lambda) = (\Lambda^{\gamma_c - \gamma} c(\gamma))^{1/1+\gamma},$$

where $\gamma < 0$, it follows that

$$A(\gamma, \Lambda)^{1+\gamma} = \Lambda^{\gamma_c - \gamma} c(\gamma),$$

where

$$c(\gamma) = \left[\int_0^\infty t^\gamma dt \left(\frac{1}{t} - \frac{1}{e^t - 1} \right) \right].$$

Hence,

$$Z|_{\gamma \rightarrow -1} = \frac{\zeta(2+\gamma)}{\rho_B^{|\gamma|}\zeta(2+\gamma_c)c(\gamma)\Lambda^{\gamma_c+1}}.$$

The expression $c(\gamma)$ tends as $\gamma \rightarrow -1$ to $(1/2) \log \varepsilon$, where ε stands for the lower limit of the integral expression for $A(\gamma)^{1-|\gamma|}$ at $\gamma = -1$.

Similarly, the expression $\zeta(\gamma+2)$ at $\gamma = -1$ is equal to $\log \varepsilon$.

Hence

$$Z|_{\gamma \rightarrow -1} = \frac{2}{\rho_B \zeta(\gamma_c + 2) \Lambda^{\gamma_c + 1}}$$

as $\gamma \rightarrow 0$ and $Z \rightarrow 0$. Therefore,

$$Z < Z_{\max} < \text{const}$$

for all values of γ .

Hence, by (65),

$$P_r = Z \rho_B T_r \left(1 - \frac{T_r}{T_B} \right) \leq Z_{\max} \frac{T_B}{2}. \quad (68)$$

Moreover, it is clear that $P_r \rightarrow 0$ as $T_r \rightarrow 0$ and $\gamma \rightarrow 0$.

The value of λ determines the minimum of P_r . On the other hand, we can calculate the value of λ if we know the value of the triple point on the binodal.

Thus, the value of $\min P_r$, which is a new critical point in the thermodynamics of transition of liquids to the dispersed phase, can uniquely be defined by the value of the critical point Z_c , the Zeno line, and the triple point.

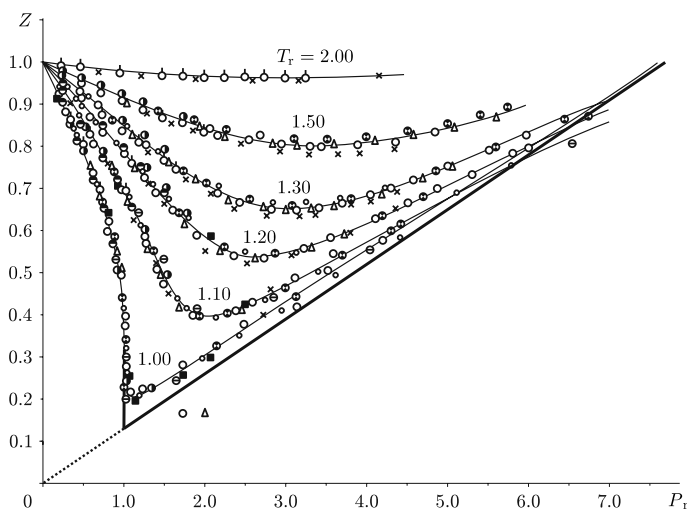


Fig. 9. The picture of the law of corresponding states for molecules of different gases. Thin lines show isotherms for methane. Different symbols on isotherms correspond to argon, carbon dioxide, water, etc. The fact that isotherms of different gases are close to one another illustrates the empirical law of corresponding states. The theoretical isotherm (the solid line) does not fully coincide with the experimental one. This is an effect of the same type as the jump of the critical exponents. The viscosity (the Wiener quantization) smooths the sharp angle of the limit isotherm (as $\varepsilon \rightarrow 0$).

3.5. A coarser measuring instrument and the law of corresponding states

When introducing the concept of observable quantity in equilibrium thermodynamics, one must keep in mind the fact that the observation itself should be carried out in discrete intervals of time that are widely separated from one another. When standing on a purely mathematical point of view, one must agree that the processes of establishing an equilibrium require infinite time. However, in mathematics there are some concepts which are similar to the notion of “half-life” in physics. For example, one can introduce a time interval during which the difference between the current state and the state of equilibrium in the course of relaxation becomes e times less.

In approximation theory and in the theory of numerical methods, especially after the well-known paper of Mandel'shtam and Leontovich [39], the following relaxation process was in use: at first, a reacting system is brought to some equilibrium. Then one rapidly changes one of the conditions

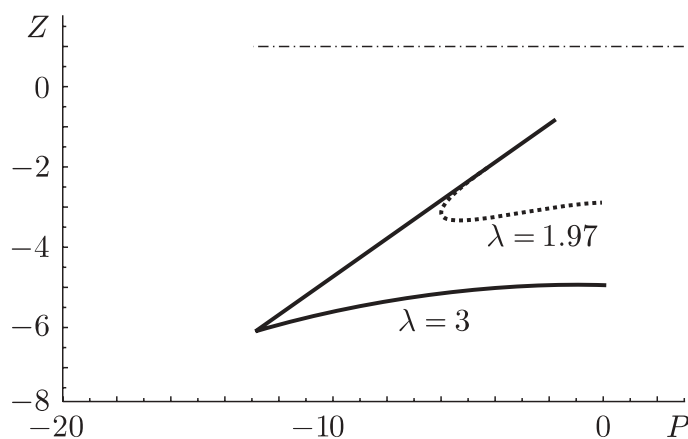


Fig. 10. Spinodal curves in the domain $P < 0$. The inclined line is the continuation of the theoretical critical isotherm shown in Fig. 9 to the domain of negative values of P and Z . The initial point of the curve $\Lambda = 1/3$ ($\lambda = 1/\Lambda$) is at a distance from the point $P = 0$, and the starting point $\Lambda = 0.5086$ ($\lambda = 1/\Lambda = 1.97$) of the curve coincides with the point of intersection of the dashed line and the solid line.

(e.g., the temperature or the pressure) and traces the evolution of the system towards a new equilibrium (see, for example, the article “method – relaxation” in the Great Encyclopedia of Oil and Gas, <http://www.ngpedia.ru> [in Russian]).

Since the observation intervals should be “equal” to the relaxation time, they are large enough, and one can refer to the process as the *multi-step relaxation process*. Economic and historical processes, and also biological processes in a living organism, belong to phenomena of this kind, and therefore, from time to time, thermodynamic models of these processes arise.

The fact that time intervals of observation are discrete is the most important point to be taken into account when speaking about the instruments of observation.

The formation of clusters, according to the scheme suggested in Sec. 3.2, can serve as an example of a multi-step relaxation process. Namely, after the formation of a dimer at $T \leq T_c$, one should consider a collision of a dimer with a monomer according to the same scheme, assuming that the pair-dimer (a μ -particle) has already been formed. Further, one considers the scattering problem again, however, for the dimer with $E_{\min} = T$ and a particle of the same mass m . The consideration of the scattering problem in succession, i.e., a step for $-\infty \leq t \leq +\infty$, and then a new step, with regard to the fact that the density does not depend on the permutation of the steps, gives a rigorous result which was announced in Sec. 3.2 by using empirical considerations, including the reason that “otherwise, there would be no liquid phase at all (if three-dimensional clusters were not formed).”

The *multi-step relaxation process* mentioned above is too cumbersome to be presented here in detail.

Obviously, the rougher is the device, the greater is the dissipation parameter, and therefore the more important is the uncertainty principle. If our device does not distinguish some molecules from one another, then this is a rough instrument. It is not necessary that the device itself be so rough. It is sufficient to say that the experimenter does not want to distinguish molecules and computes the density roughly, counting all the molecules for which he wants to construct a “rough” thermodynamics. Hence, when speaking more precisely, from the point of view of mathematics, the rougher thermodynamics we want to receive, the more rough will be the answer due to the Wiener uncertainty principle.

Our rough instrument does not distinguish particles not only in mixtures. Measuring different particles, the observer thinks that these are the same molecules, and only the measurements are somewhat scattered. This is even a more rough thermodynamics. It is referred to the fluid part, when the gas-liquid is not distinguished, clusters occur, etc. The critical points are on the boundary of the fluid domain, and we approach them from the side of the fluid domain for $T \geq T_c$.

When considering above the phase transition, we have equated the chemical potentials of the liquid and the gas phases on the critical isotherm, assuming that there is no phase transition there. We considered the case in which the viscosity vanishes, and we obtained a phase transition which

was not smeared. Now, when considering the problem with a coarser device, we no longer have any right to assume that the dissipation tends to zero. The uncertainty principle gives us a fairly large smearing of the phase transition; however, it happens on a “rough” critical isotherm which is measured by a rough instrument. The latter cannot distinguish now not only particles of a single pure gas but does not distinguish particles of different gases either.

We have compared the Wiener quantization of thermodynamics with the dissipation resulting in a shock wave. However, the dissipation may be different in different substances, while we are interested now in the Hugoniot conditions for the entire mixture, and we do not want to distinguish stratificationally occurring internal shock waves within a common shock wave. This is particularly evident when the dissipative parameters of viscosity and thermal conductivity are different (see [40], § 95), the viscosity ν is small, and the thermal conductivity is relatively large, $\chi \gg \nu$. If the processes inside the shock wave are not of interest for us, then we pose the Hugoniot conditions on a shock wave spread with respect to heat conductivity.

On the other hand, if the values of viscosity in a mixture of different gases are different but not dramatically different from one another, then the width of a shock wave thus obtained is defined by the average viscosity.

Since, as a rule, the Bose-Einstein distribution is considered in the three-dimensional case, it would seem to be natural to add the integration over the coordinates to the integration of the momenta. Then the three-dimensional volume V would occur as if this is a natural way. It would seem that there can be a generalization if the dimension of volume is changed when changing the dimension of the momenta. However, in the manual [2], when considering a photon gas, the integration of the Hamiltonian of the oscillator is carried out both over the momenta and over the coordinates, and, nevertheless, the three-dimensional volume V is taken as the multiplier for the distribution.

Note first that number theory gives, for dimension two, a distribution without the volume V (see Example 1), as well as the initial relations in [2] both for the Boltzmann–Maxwell ideal gas and for the Bose–Einstein ideal gas (see (1)–(4)). Further, in [2], both the distribution for bosons and the distribution for photons are multiplied by the three-dimensional volume V . Certainly, the main distribution is the distribution without the volume V , and its multiplication by V is caused by the correspondence with thermodynamics in which the pair ‘the volume V – the pressure P ’ is the most important tool.

Therefore, the most natural generalization to the nonideal distribution is the multiplication of a fractional Bose distribution by a function of V of the form $V\varphi(V/V_0)$, where V_0 stands for some reference volume and the function $\varphi(x)$ is smooth.

The introduction of this multiplier does not change the distribution caused by number theory [41] in which the variable V is eliminated by the change of the variable $N/V = \rho$. However, if we consider $V\varphi(V/V_0)$ as a multiplier, where V_0 is some typical volume, then the relation for the three-dimensional Lagrangian manifold Λ^3 in the six-dimensional phase space $\{P, V; T, S; \mu, N\}$ is preserved, whereas the variables V and N do not convert here into a single variable $\rho = N/V$. Therefore, the volume and the number of particles are changed on the isochore $\rho = \text{const}$ in general. This modification of the Ω -potential does not change the specific entropy, which is also of importance.

In a mixture of gases, we are to choose a reference gas in which the difference between the vapor and the liquid is the lowest possible, for example, from the point of view of the number of dimers. This gas is the mercury vapor ($Z_c = 0.4$). Let us carry out a normalization of activity (26) for an isotherm of this gas at $Z = 0.4$ and assume that there is no phase transition on the critical isotherm of mercury. In accordance with what was said above, the rough device cannot distinguish among molecules of l distinct gases. Let us calculate the average degree of freedom for these molecules by taking the arithmetic mean of the values of the entropy of l pure gases on the basis of experimental data for Z_c^i , $i = 1, 2, \dots, l$, pure gases (see (13)),

$$(\gamma_{average} + 2) \frac{\zeta(\gamma_{average} + 2)}{\zeta(\gamma_{average} + 1)} = Z_{average}(\gamma_{average} + 2) = \frac{1}{l} \sum_{i=1}^l (\gamma_i + 2) \frac{\zeta(\gamma_i + 2)}{\zeta(\gamma_i + 1)}.$$

The highest value $Z_c = 0.4$ is given by mercury (Hg), and therefore the average number of degrees of freedom of this family of molecules is certainly less, and therefore $Z_{average} < Z_c$ (mercury), $\gamma < \gamma_{Hg}$. The critical pressure is greater than that for mercury, $\zeta(\gamma_{Hg} + 2) < \zeta(\gamma_{average} + 2)$. Therefore, the

value we have chosen for mercury, $P_r = 1$, is less than $P_{average} = \zeta(\gamma_{average} + 2)/\zeta(\gamma_{Hg} + 2)$. Thus, the value $P_r = 1$ for Z_{Hg} belongs to the domain of the phase transition “gas-liquid” for $Z_{average}$. This implies that, for $P_r = 1$, the phase transition to liquid occurs at $Z_{average}$.

This phase transition to liquid can be seen in Fig. 9, in the form a vertical bounded by a black sloping line depicting the liquid⁹.

Taking into account the Zeno line influences the form of the Ω -potential as follows:

$$\Omega(\mu, T) = -\Lambda^{\gamma+1} V \varphi(V/V_0) \frac{T^{\gamma+2}}{\Gamma(\gamma+2)} \int_0^\infty \frac{t^{\gamma+1} dt}{(e^t/y) - 1} = -\Lambda^{\gamma+1} T^{\gamma+2} V \varphi(V/V_0) \text{Li}_{\gamma+2}(y), \quad (69)$$

where $y = \exp(\mu/T)$ is the activity and μ stands for the chemical potential.

Let us write out the differential equations for $\varphi(x)$ with regard to the relations on the Zeno line,

$$T_z = T_B (1 - \rho_z/\rho_B), \quad P_z = \rho_z T_B (1 - \rho_z/\rho_B), \quad (70)$$

where the subscript z means that the corresponding values are taken on the Zeno line, i.e., for $Z = 1$.

Let us construct the relation $Z = 1$ on the Zeno line. This relation is of the form

$$Z = \frac{\partial \Omega / \partial V}{T_z \partial \Omega / \partial \mu} = \frac{\varphi(V_z/V_0) + (V_z/V_0) \varphi'(V_z/V_0)}{\varphi(V_z/V_0)} \cdot \frac{\text{Li}_{\gamma+2}(y_z)}{\text{Li}_{\gamma+1}(y_z)} = 1. \quad (71)$$

It follows from (70) on the Zeno line that

$$T_z^{2+\gamma} [\varphi(V_z/V_0) + (V_z/V_0) \varphi'(V_z/V_0)] \text{Li}_{\gamma+2}(y_z) = (N/V_z) T_B (1 - N/(V_z \rho_B)). \quad (72)$$

Assume that the conditions $N/V = \text{const}$ and $N = \text{const}$ hold on the isochore and on the Zeno line defined by relation (70). It follows from (71) and (72) that

$$T_B^{\gamma+1} (1 - N/(V_z \rho_B))^{\gamma+1} \varphi(V_z/V_0) \text{Li}_{\gamma+1}(y_z) = N/(V_z \rho_B). \quad (73)$$

Here $N/V_z = \text{const}$ and $N = \text{const}$, and hence this equation contains unknowns y_z , V_z , and $\varphi(V_z/V_0)$.

After finding the value y_z as a function of V_z and $\varphi(V_z/V_0)$, we substitute it into formula (71), thus transforming equation (71) into a differential equation for the function $\varphi(x)$ depending on the constants ρ_B and T_B . The equation for $\varphi(V)$ enables one to find the point $y_z(\rho)$ on the Zeno line, and, after this, the isochore is changed only at the expense of the modification of activity $a = e^{-\mu/T}$ from $y_z(\rho)$ to $a = 1$ for the polylogarithm $\text{Li}_{\gamma+1}(a)$. The function $\varphi(V)$ is not reflected in the structure of the isochore, and it is reflected in scaling only (see Fig. 11, (a)).

The most important problem in the theory of differential equations, the existence problem for a solution, remains open. Physicists pay less attention to this problem than mathematicians.

What are conditions for the existence of a solution of equations (71)–(72)?

Introduce the notation $T_s = T_{\text{standard}} = T/T_m$ and $P_s = P_{\text{standard}} = P/P_m$, where T_m and P_m are defined by the formulas

$$P_m = T_m^{\gamma+2}, \quad V_0 = V_m = V_{\text{max}},$$

and $Z_m = Z_{\text{max}}$ and $\rho_m = \rho_{\text{min}}$ are defined below.

Since N_c does not depend on T , it follows that V and N are constant along the isochore $V = V_m$.

Let us write out the above relations at the point $T_s = 1$, $P_s = 1$:

$$[\varphi(V_z/V_0) + (V_z/V_0) \varphi'(V_z/V_0)] \zeta(\gamma + 2) = 1, \quad V_m \varphi(1) \zeta(\gamma + 1) = N_c, \quad V_m = V_{\text{max}}, \quad (74)$$

⁹One can rigorously prove the existence of phase transition only for the transition of a new ideal gas into a new ideal liquid without taking into account the Zeno line, which is unknown for $\gamma_{average}$. Therefore, a rigorously proven transition from $Z = 0.4$, $P = 1$ to a liquid is obtained a bit higher than at the point $Z = 0.12$, $P = 1$ in Fig. 9.

Hence,

$$Z_m = \frac{V_m \zeta(\gamma + 1)}{N_c \zeta(\gamma + 2)} \cdot \frac{\text{Li}_{\gamma+2}(1)}{\text{Li}_{\gamma+1}(1)} = \frac{V_m}{N_c} = \frac{1}{\rho_m}. \quad (75)$$

Since we construct isochores $V = \text{const}$ on the plane $\{Z, P\}$, it follows that $V_m = V_z$. Eliminating $(V_z \varphi(V_z/V_0))'$ from (74) by using (73), we obtain

$$T_B^{\gamma+1} \left(1 - \frac{1}{Z_m \rho_B}\right)^{\gamma+1} \frac{1}{\zeta(\gamma + 2)} \text{Li}_{\gamma+2}(y_z) = \frac{1}{Z_m}. \quad (76)$$

Since $V_m = V_z$, we see that

$$\varphi(1) = N_c (\zeta(\gamma + 1) V_m)^{-1}, \quad \varphi(1) + \varphi'(1) = (\zeta(\gamma + 2))^{-1}, \quad (77)$$

and it follows from (71) on the Zeno line that the following equation holds:

$$\frac{\text{Li}_{\gamma+2}(y_z)}{\text{Li}_{\gamma+1}(y_z)} \cdot \frac{V_m}{N_c} \cdot \frac{\zeta(\gamma + 1)}{\zeta(\gamma + 2)} = 1. \quad (78)$$

Eliminating y_z , we find a relation for Z_m and γ . The maximum value of Z_m depends on the values of ρ_B and T_B only. For mercury, this maximum is obtained for $\gamma_m = \gamma_{\min} = 0.1$, and $Z_m = 0.4$, which coincides with the value of Z_c for mercury. This coincidence, which depends on ρ_B and T_B , holds for mercury Hg only (among all the elements of the periodic table), which confirms the correct choice of the Ω -potential (69).

The family of isochores, according to system (72)–(73) with the above initial condition (77), is shown in Fig. 11 (b).

The first relation for the limit isochore $V_m/N_c = Z_m$, for $\gamma = \gamma_m$, is of the form

$$Z = Z_m \cdot \frac{\zeta(\gamma + 1)}{\zeta(\gamma + 2)} \cdot \frac{\text{Li}_{\gamma+2}(y)}{\text{Li}_{\gamma+1}(y)}, \quad 1 \leq y \leq y_z(\gamma). \quad (79)$$

Since $P_s = T_s^{\gamma+2} \text{Li}_{\gamma+2}(y)/\zeta(\gamma + 2)$ and $N = T_s^{\gamma+1} \text{Li}_{\gamma+1}(y)V_m$, it follows that the other relation is

$$P_s = \left(\frac{\zeta(\gamma + 1)}{\text{Li}_{\gamma+1}(y)}\right)^{(\gamma+2)/(\gamma+1)} \frac{\text{Li}_{\gamma+2}(y)}{\zeta(\gamma + 2)}, \quad 1 \leq y \leq y_z(\gamma). \quad (80)$$

Equations (79) and (80) give an almost straight segment of the isochore.

Starting from $Z < 0.4$ (for example, for a van der Waals gas), the phase transition to a liquid occurs for indistinguishable particles of the law of corresponding states. This gives a broad area (at the expense of the uncertainty principle of a “rough device”) around the line segment $P = 1$, $T_s = 1$, $Z < 0.4$.

Remark 5. Since the rightmost isochore (which is not shown in Fig. 11) is a segment of a straight line, it follows that all isochores of high density must also be line segments. They pass through the point $\rho > \rho_m$ on the Zeno line and the point $Z_0 = 1/\rho$ on the line $P_s = 1$. We thus obtain (when including the isochores shown in Fig. 11) a complete family of isochores for $Z \leq 1$, $P \geq 1$, related to the law of corresponding states. To any point of an isochore in the plane $\{Z, P\}$ there corresponds a point of temperature, and we construct isotherms which, up to the Wiener uncertainty principle, correspond to the experimental law of corresponding states (Fig. 12).

In Fig. 13, the graph of an experimental isotherm for mercury is presented; this graph was kindly evaluated by Professor V. S. Vorob'ev, according to the most recent data, at the instance of me. Note that the passage gas–liquid happens at $T = 1473 \text{ K}$ along a slanting line rather than a vertical one, which is related to nonzero viscosity and the Wiener uncertainty principle. This effect is of the same nature as the jump of critical exponents and “thickness of the layer” of a shock wave.

classic; $V=0.5, 0.6, 0.8, 1, 2$

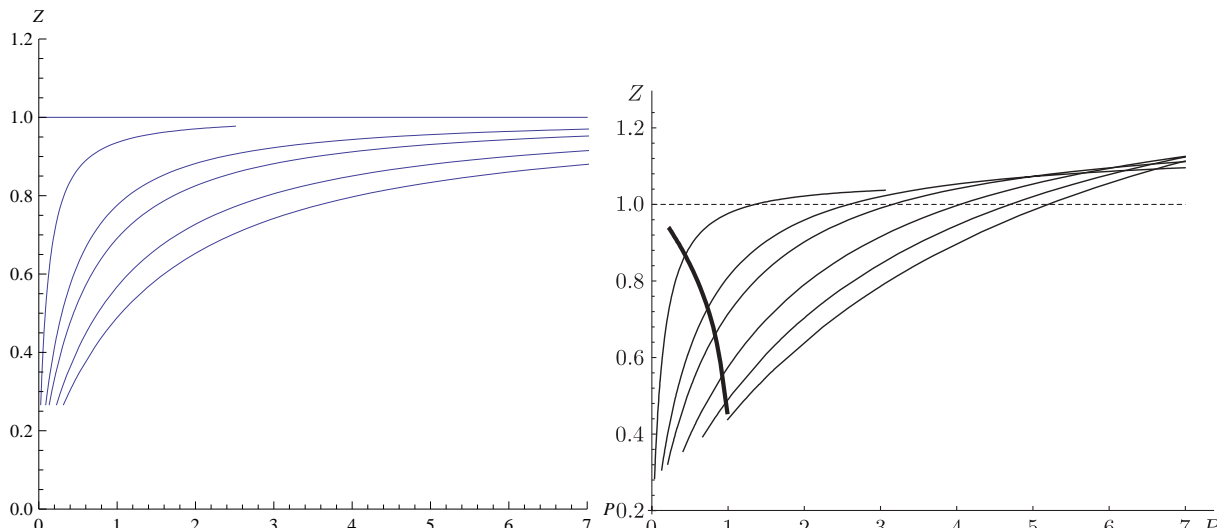


Fig. 11. (a) The graph for the isochore of the polylogarithm $\text{Li}_{\gamma+1}(a)$ for $\gamma = 2$. (b) The dotted line shows the Zeno line $Z = 1$. The bold line is the critical isotherm of a real gas (mercury) which is calculated theoretically, and the fine lines are isochores of mercury for $T < T_c$.

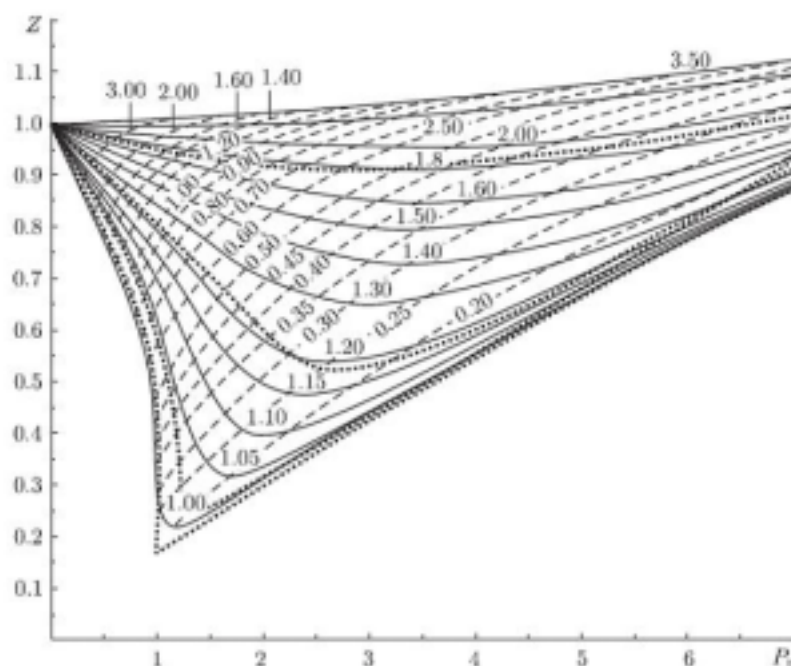


Fig. 12. The thin solid lines represent the experimental isotherms for methane (see Fig. 9). The dotted lines approximating the experimental curves are based on theoretical data. The dashed curves show the experimental isochores.

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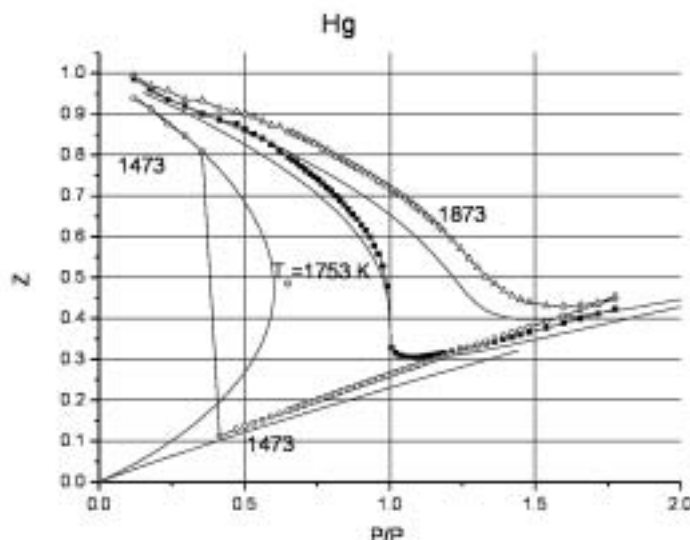


Fig. 13. The Hougen–Watson diagram for mercury. Experimental data (from the sources W. Gotzloff, G. Schonherr, F. Hensel, *Z. Phys. Chem. Neue Fol.* **156** 219 (1988) and W. Gotzloff, Ph. D. Thesis, University of Marburg, 1988) are equipped with symbols. The thick lines correspond to the van der Waals equation for the related temperatures.

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