
Ideal Gas/Liquid Transition as a Generalization of the Problem of “partitio numerorum”

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Abstract. It is shown that the Boltzmann–Maxwell distribution is not applicable to the generalized notion of ideal gas and corresponds to this ideal gas at low density only. The behavior of an ideal gas and its transition to liquid is studied as a result of a kind of generalization of the problem of “partitio numerorum”. The reflection of particles of the ideal gas from the walls of the vessel walls is taken into account (as a kind of “trap” for the Bose gas). Two constants are additionally introduced, namely, the constant Λ inversely proportional to the mass and the heat g of the phase transition as $T \rightarrow 0$ (the constant of the Clausius–Clapeyron relation), and also the experimental value of the critical compressibility factor for the given gas and the experimental value of the pressure at the triple point, from which one can find the value of the constant Λ .

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Yurii Ivanovich Manin, a famous mathematician, is at the same time a philosopher who tries to reach the heart of science from the point of view of abstract mathematics and mathematical logic. His forecast concerning quantum computers [1] has largely been confirmed in the fundamental works of A. Kitaev.

In the present paper, we show that Manin’s prediction concerning number theory and its role in physics¹ has also been justified. The actual generalization of the famous problem of partitio numerorum, carried out by Vershik, became the basis of the mathematical explanation of such an old “mysterious” phenomena as the vapor-liquid transition. As can be seen by the example of decomposing a number M into n summands, adding a zero to the list of possible values of the summands used in the old formulation increases the number of versions for the decomposition. If the zero value is excluded from the summands, then the decomposition of the number 5 into two summands has two possibilities, $5 = 2+3 = 1+4$; however, after the introduction of the zero value, the third possibility arises, namely, $5+0$, i.e., a version of decomposing 5 is added. Thus, adding zero to possible values of the summands enables one to join all versions of decomposing M into $s < k$ summands and then to add the zero summands. Thus, the zero value gives a nondecreasing number of versions as k increases. For some $k = k_0$, the number of versions stops its growth, and therefore, for $k > k_0$, only the number of zeros increases. This is an example of the so-called Bose condensate phenomenon in quantum statistical physics.

If a partition

$$M = a_1 + \dots + a_N$$

of a number M into N summands is given, then, denoting by N_j the number of summands that are precisely equal to the number j on the right-hand side of this equation, we see that the sum of summands equal to j is equal to jN_j , because there are N_j summands of this kind, and then the

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¹In [2], Manin wrote: “there is a clearly discernible trend to at least admit number theory in the world of ideas of modern theoretical physics” (p. 209).

sum of all summands is obtained by summing these expressions for all j , i.e., it is equal to $\sum_j jN_j$ on one hand and M on the other hand. Hence,

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

The total number of summands is equal to $\sum_j N_j$, and this number is equal to N because we know that the total number of summands is equal to N ,

$$\sum_{i=1}^{\infty} N_i = N. \quad (2)$$

These two conditions are analogous to the two conditions for the energy \mathcal{E} and the total number of particles N appearing [3]. The volume V does not enter these conditions.

Remark 1. However, is it true that the extra particles are accumulated for $N > N_c$ at the very point $i = 0$? In fact, the question is as follows: whether or not the number of zeros in the above problem is much greater than the number of units as $M \rightarrow \infty$, i.e., whether or not the relation $N_1 = o(N_0)$ holds even for $N > N_c$?

The computer simulation gives a negative answer. Experts in number theory also answer negatively. Especially for $D > 2$, in which case the Euler–Maclaurin estimates can already be applied and, for $i \gg 1$, we can pass to the integral, it is impossible to talk about a single point $i = 0$, as in the handbook [3].

In fact, together with the convergence of the integral (for example, in the three-dimensional case) as $N \rightarrow \infty$ and $\mu \rightarrow 0$, the bell-type function $\sqrt{N}e^{-Nx^2}$ also increases, where

$$\frac{1}{\ln N} > x \geq 0 \quad (3)$$

(cf. [4]).

The analogy with saturated vapor above a liquid is clear: reducing the volume of the vessel does not affect the density of steam, and the extra particles (as the volume decreases) settle to the fluid, in just the same way as above, in the case of $k > k_0$.

The word “condensate” is used both in Bose statistics and in the vapor-liquid system. However, the fact that, mathematically, this is one and the same phenomenon in essence, and that this approach leads to new formulas which are experimentally confirmed, has been, speaking mildly, puzzling theoretical physicists, who have understood this in a different way for 200 years.

Below we speak of an “ideal” or “perfect” gas, i.e., a gas “without interaction,” which means in reality, above all, without any potential ensuring an attraction between the particles² The old axiom claiming that “there can be no liquid without an attraction” is destroyed.

²Cf. the article “Ideal gas” in <http://ru.wikipedia.org>: “Ideal gas is a mathematical model of gas which suggests that the potential energy of interaction of the molecules is negligible as compared to their kinetic energy. No forces of attraction or repulsion act between molecules, the collisions between particles and *with the walls of the vessel are absolutely elastic* (my italics, VM), and the time of interaction between the molecules is negligible as compared with the average time between the collisions.” In http://en.wikipedia.org/wiki/Ideal_gas, the text is softer: “In physics, a perfect gas is a theoretical gas that differs from real gases in a way that makes certain calculations easier to handle. Its behavior is more simplified compared to an ideal gas (also a theoretical gas). In particular, intermolecular forces are neglected, which means that one can use the ideal gas law without restriction and neglect many complications that may arise from the Van der Waals forces.” In http://en.wikipedia.org/wiki/Perfect_gas, the text begins as follows: “In physics, a perfect gas is a theoretical gas that differs from real gases in a way that makes certain calculations easier to handle.”

At a certain temperature and pressure, an ideal gas forms a liquid. This follows from some generalizations of number theory. However, a while ago, a well-known physicist told me: “your lemmas do not convince me,” and thus the author is now trying to write his text in such a way that it will convince physicists without formulating lemmas and theorems. First of all, let us ensure that the distributions of classical particles are also symmetric with respect to any permutation of coordinates (and also of momenta).

In physics, the relationship between the Bose–Einstein distribution and number theory was first noticed by Temperley. For the mathematical background, see [5, 6]. Roughly speaking, the invariance of quantum equations, according to the “principle of indistinguishability of identical particles” [3], is equivalent to the statement “any permutation of the summands does not change the sum.”

However, the initial conditions in the classical Hamiltonian system for N particles need not be invariant under all permutations of the particles, even if the Hamiltonian itself has this invariance property. Nevertheless, one may assume that the initial conditions of the Liouville equation satisfy the symmetry conditions.

Indeed, suppose that

$$\{q_i^0, p_i^0\}, \quad (q_i^0 = q_{i,1}^0, q_{i,2}^0, q_{i,3}^0, \quad p_i^0 = p_{i,1}^0, p_{i,2}^0, p_{i,3}^0) \quad (4)$$

are the initial values for a Hamiltonian system whose Hamiltonian commutes with any transposition of p_i, p_j and with any transposition of q_i, q_j . For example,

$$H(p, q) = \sum \frac{p_i^2}{2m} + \sum \sum V(|q_i - q_j|). \quad (5)$$

Substituting the initial values into the Hamiltonian (5), we obtain the energy

$$E = H(p_i^0, q_i^0). \quad (6)$$

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

Further, consider the Liouville equation corresponding to the Hamiltonian system,

$$\frac{\partial \rho}{\partial t} = \{H(p, q), \rho\}, \quad (7)$$

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

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

where E satisfies (6). This equation describes the distribution corresponding to the Hamiltonian system and satisfying the above initial conditions.

The Liouville equations and their initial conditions are symmetric with respect to the permutations both of p_i and p_j and of q_i and q_j . This symmetry is preserved for solutions. According to the Gibbs distribution, for the Gibbs Ensemble, every distribution can be expressed by using the energy. Therefore, it is symmetric with respect to any permutation of the particles.

Schoenberg carried out the second quantization of this system in the Fock space. The author obtained the Vlasov equation from this quantization, 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, a symmetry of this kind follows. Thus, we come to the commutativity of the particles, and thus to the Bose–Einstein-type distribution for the statistical physics of classical particles. Other mathematically

rigorous arguments which lead to a distribution of the Bose–Einstein-type, in the form of lemmas and theorems (see [7]), obey the laws of number theory, and hence so are also the distributions of classical particles.

The construction presented in [8] avoids the use of the volume V and uses only two relations, without involving anything else. One will be able to speak of whether or not this construction describes the classical ideal gas only if we shall define what the term “ideal gas” means more precisely³.

Physicists usually say that an ideal gas has no interaction. However, what does these words mean?

Particles collide with one another as balls of a very small radius having a sufficiently high density. The average density (the concentration) is the number of particles in the vessel divided by the volume of the vessel. Moreover, the particles are reflected from the walls of the vessel.

We can note the following facts: 1) there is no attraction in an ideal gas; 2) the vessel is closed, and the number of particles in it is preserved.

a) Consider the example of repulsion between the dust charged by some charge and the walls of the container that are charged with the same charge and repel the dust. This vessel is referred to as a trap. If the vessel is rectangular, then, under some special conditions, the charged dust can form a crystalline structure. Under some other special conditions, the dust melts and becomes a liquid. If one opens the vessel, then the above structure collapses rapidly (and the dust is smashed), because there is no attraction and there is only repulsion. This is a very rough interpretation of a well-known experiment, and this interpretation is confirmed by methods of molecular dynamics [9] (see also [10]).

b) The Boltzmann–Maxwell ideal gas corresponds to the relation

$$PN = NT. \quad (8)$$

This relation follows from the Boltzmann distribution, in which every permutation of two particles (balls of the same mass and the same radius) gives a new state. For the balls of not very small radius, the so-called Maxwell distribution is obtained after 2–3 collisions.

It is assumed that the same result can also be obtained in the case of a large number of balls of small radius. It turns out here that relation (8) is invariant with respect to the number of degrees of freedom, i.e., a “spherical” molecule can consist of several atoms, the number of degrees of freedom can be large, and still the relation (8) is preserved. The collisions with the boundary of the vessel are neglected.

c) The Maxwell distribution corresponding to the Boltzmann distribution also involves the mass of a particle (as an additional constant preserving relation (8)). By Courant’s classical formula, the number of eigenvalues that are less than a given value $\lambda \gg 1$ (the spectral density $\rho(\lambda)$) has the asymptotic behavior

$$\rho(\lambda) = \frac{Vm^{D/2}\lambda^{D/2}}{\Gamma(D/2 + 1)(2\pi)^{D/2}\hbar^D}(1 + o(1)) \quad \text{as } \lambda \rightarrow \infty \quad (9)$$

(V stands for the D -dimensional volume).

Relation (8) holds very well under normal conditions, i.e., at the pressure of 1 bar and at “room” temperature. The molecules are also rather free under these conditions, and therefore the number of degrees of freedom is an integer.

As was indicated in [3], in the case of symmetry with respect to permutation of particles in the three-dimensional case, the adiabat coincides with the Poisson adiabat the monatomic gas.

³The definition used by the Russian Wikipedia and cited in the previous footnote coincides largely with the concept of the author.

However, such a symmetry reduces the number of degrees of freedom, and this number is no longer integer in general.

If we pass to the van der Waals normalization

$$T_r = \frac{T}{T_c}, \quad P_r = \frac{P}{P_c}, \quad (10)$$

then Λ , as well as the mass, disappears for gas. This means that, under this normalization, there remains a dimensionless parameter $\Lambda^{\gamma-\gamma_c}$ (Λ is inversely proportional to the mass of a particle), which becomes equal to one for $\gamma = \gamma_c$.

It is in general inessential to list other parameters to be included into the value of Λ to make it dimensionless. To avoid thinking what are the parameters to be used (e.g., viscosity or \hbar), one can choose the mass of a particle and normalize with respect to this mass. This reduced mass becomes a normalization in the spirit of van der Waals. However, it must be necessarily multiplied by a constant, because, for liquids, the constant Λ plays a significant role in the phase transition and is determined from the condition that the pressure coincides with the experimental value at the triple point. Hence, the value of this constant is significant also for the gas-liquid phase transition. In chemical thermodynamics, for solutions, there is the so-called “law of mass action,” which also shows the importance of this constant $\Lambda^{\gamma-\gamma_c}$ (see [11]) in the case of new liquids satisfying the symmetry condition for the permutations.

d) If the temperature and density are reduced for the Boltzmann–Maxwell ideal gas, then another phase necessarily occurs, which can be liquid or solid (a crystal).

In this case, another constant is introduced in the theory of an ideal gas–vapor as $T \rightarrow 0$, namely, the value q of the latent heat of transition from the gaseous phase to liquid or solid. This value is different for different gases.

In the ideal case “gas–liquid” considered above, the liquid does not disappear (as is the case in the case a)) after opening the bottle. This new phenomenon is due to the Bose condensate phenomenon, which, as we shall show below, holds for big agglomerations of classical particles of small radius.

Let us present an analog of Bose condensate.

If one throws salt into a saturated salt solution, involving strength, and mixes, involving strength, then, in some time, other particles will fall out in the sediment and will (relatively) easily lie on the bottom, unlike the molecules of the liquid.

In fact, relation (8) contains three variables, because N/V is the concentration, which can be measured, in contrast to the number of particles in the vessel. Multiplying the concentration by the mass m of a particle, we obtain the density $\rho = mN/V$. This quantity can be measured in even a simpler way than the concentration. Therefore, relation (8) can be represented as

$$P = \rho T. \quad (11)$$

Moreover, for a sufficiently rarefied gas and for low gas densities, the particles collide less frequently, and, for low temperatures (i.e., for low speeds of the molecules), the collision with the walls of the vessel plays a more significant role. In addition, another phase necessarily arises, liquid or crystal, and there is a Clapeyron–Clausius law of exponential dependence of the pressure on temperature, of the form

$$P = \text{const } e^{-\text{const}/T}. \quad (12)$$

Remark 2. Theoretical physicists have yet another standard dictum: for an ideal gas (for the definition, see above, and see also <http://ru.wikipedia.org>), one can neglect the reflection from the boundaries of the vessel, it is inessential, and the behavior of particles of the gas does not depend on their location within the vessel⁴.

⁴Cf. the sentence about residence registration in my book [21].

However, for the case in which the gas is so rarefied that the mean free path is so large that the particles collide rarely we have the so-called Knudsen criterion. Certainly, in this case, this is not a gas, and these are not chaotic collisions.

Of course, this is not a phase transition “gas–Knudsen”; this is a gradual increase of the role of repulsion from the border as the density decreases. In fact, it is taken into account by physicists in the so-called Clapeyron–Clausius law. This law claims that the asymptotic behavior of the pressure P as $T \rightarrow 0$ is of the form [3]

$$P \sim e^{-q/T}, \quad (13)$$

where q is the heat of the transition vapor–liquid as $T \rightarrow 0$.

Physicists will say here that this is already not an ideal gas in its “ideal understanding,” and here we have two phases, the vapor–liquid. Although the vapor satisfies equation (8) for an ideal gas, this is only another random coincidence. Yes, the vapor density is small, but the Knudsen criterion can be applied in a different situation only.

However, we shall show in another paper that the actual collision with the boundary (the existence of this collision is mentioned in the very definition of an ideal gas in the Russian Wikipedia) leads to the Clapeyron–Clausius law, because the gas cannot exist without the presence of another phase as $T \rightarrow 0$; conversely, for an arbitrarily small temperature, in a closed vessel, there is a vapor of small density (along with liquid or solid phase).

e) Thus, in the case of an ideal gas, i.e., a gas in which there is a repulsion from the boundary of the vessel and the repulsion between the infinitely small balls, we introduce three additional parameters that characterize the *given* gas. Namely, the first two parameters are the mass m and the fractional number of degrees of freedom D , which can be defined from the experimental value of the critical compressibility factor

$$Z_c = \frac{P_c V_c}{T_c N_c} = \frac{\zeta(2 + \gamma_c)}{\zeta(1 + \gamma_c)} \quad (14)$$

for the given gas, where ζ stands for the Riemann zeta function and γ_c for the critical value of gamma, and the number of degrees of freedom is defined by the relation

$$D = 2\gamma + 2. \quad (15)$$

In particular, to dimension 3, there corresponds $\gamma_c = 1/2$ and, to dimension 2, there corresponds the value $\gamma_c = 0$.

The third constant is the heat of the phase transition, q , as $T \rightarrow 0$.

Remark 3. It is difficult to implement such a situation experimentally. As is well known, each molecule can be regarded as a dipole. The dipole-dipole interaction is studied in quantum mechanics, and it mainly uses the exchange mechanisms, i.e., the symmetry with respect to permutations. In this sense, it is almost impossible to separate, in the statistical case, a large number of classical particles of small radius that commute in the distribution from quantum-mechanical particles in the equations for the distribution. Moreover, the principle of symmetry with respect to permutations for the distribution of electrons and nuclei can possibly lead in the classical consideration to the attraction of classical molecules which is similar to the one-dimensional attraction of Bose particles in the quantum case; however, as an interaction with the nearest neighbor.

f) In our case, we consciously and fundamentally neglect the geometry of the boundary of the volume V . There is a sufficiently large volume V , and the problem should be invariant with respect to changes in its shape. There is no external field in our problem, and therefore the single-particle potential in the Gibbs distribution (in the Gibbs ensemble, see [13]) must be represented, for an

infinitely small radius of molecules, in the form $\varphi(r^3/V)$, $\varphi \in C^\infty$. However, since the volume is large, the leading term is of the form

$$-\frac{\alpha r^3}{V}, \tag{16}$$

where α is a parameter that can be expressed by using the parameter q , as we shall see below. This dependence arises by the invariance with respect to the shape of the vessel of the volume V . We have no linear parameter with respect to coordinates.

To define the additional parameters, it is sufficient to take the volume in the form of a ball of radius R , because these parameters should be independent of the shape of the vessel.

We replace the parameter of an integer number of degrees of freedom by a continuous parameter characterizing the given molecule. In principle, this parameter γ has the same physical origin as the number of degrees of freedom. However, since it is continuous, it takes into account the spectrum of the molecule more subtly.

The dimensionless parameter Λ is inversely proportional to the mass. The other quantities used to make the mass dimensionless are not significant.

We have the energy

$$\mathcal{E}_r = \frac{p^2}{2m} + C \frac{r^3}{R^3}.$$

According to the integral of the Gibbs distribution, we obtain

$$\int_{R_1}^R \int_{|p| \geq 0} e^{\frac{-p^2/2m - Cr^3/R^3 + \mu}{T}} dr^3 d|p|^3, \tag{17}$$

where $R_1 = R(1 - \varepsilon(1 - T_r^l))$ (ε stands for the layer thickness number and l is constant), which leads to the Clapeyron–Clausius law as $T \rightarrow 0$.

If we neglect the influence of the walls of the vessel, then the isotherm of the ideal gas, under the assumption (14), has the following form in the (P, Z) plane:

$$P_r = T^{2+\gamma_c} \frac{\text{Li}_{2+\gamma_c}(a)}{\zeta(2+\gamma_c)}, \quad Z = \frac{\text{Li}_{2+\gamma_c}(a)}{\text{Li}_{1+\gamma_c}(a)}, \quad a = e^{-\mu/T}, \quad \mu \leq 0 \tag{18}$$

(see the graphs in [11]).

Taking the potential r^3/V into account changes the pressure and the compressibility factor Z . This enables one to consider the reflection of the walls of the vessel in a general form. We have

$$\int_{R_1}^R e^{-r^3 Ck/R^3} dr^3 = \frac{R^3}{Ck} \int_{kCR_1/R}^{kC} e^{-x} dx. \tag{19}$$

This shows that the k th term in the definition of polylogarithm for the Bose distribution with a fractional number of degrees of freedom,

$$\text{Li}_s(a) = \sum_{k=1}^{\infty} \frac{a^k}{k^s},$$

becomes

$$\frac{e^{Ck/T} - e^{(Ck/T)(1-\varepsilon(1-T_r^l))}}{Ck^{3+\gamma_c}}.$$

Hence,

$$P = -\frac{T^{3+\gamma_c}}{C} \left\{ \text{Li}_{3+\gamma_c}(ae^{-C/T}) - \text{Li}_{3+\gamma_c}(ae^{-C/T\{1-\varepsilon(1-T_r^l)\}}) \right\} \cdot \text{const} \tag{20}$$

and

$$Z(a, T) = \frac{\text{Li}_{3+\gamma_c}(ae^{-C/T}) - \text{Li}_{3+\gamma_c}(ae^{-C/T\{1-\varepsilon(1-T_r^l)\}})}{\text{Li}_{2+\gamma_c}(ae^{-C/T}) - \text{Li}_{2+\gamma_c}(ae^{-C/T\{1-\varepsilon(1-T_r^l)\}})}. \quad (21)$$

Note that $Z(1, T_c) = Z_c$ (see (14)). The constant in (20) is chosen according to the van der Waals normalization condition (10). The potential term is neglected here in the definition of pressure. For the justification, see [26]. Since, according to formulas of Bose–Einstein type, sums of the form

$$\sum_{i=0}^{\infty} \lambda_i N_i = M, \quad \sum_{i=0}^{\infty} N_i = N,$$

can be replaced by integrals, it is impossible to actually distinguish the point $i = 0$, and the condensation phenomenon can occur in an entire neighborhood of this point rather than at the only point $i = 0$ itself. However, for $D \leq 2$, the Euler–Maclaurin formula cannot be applied (i.e., one cannot pass from sums to the corresponding integrals), and therefore the point $i = 0$ can be distinguished indeed.

The liquid phase corresponds to $T < T_c$ and, in the ideal case, it corresponds to the number of particles N which cannot be increased due to the phenomenon of Bose condensation. Therefore, the isotherms of the liquid phase in the (Z, T) diagram are straight lines passing from the point at which the gas isotherms correspond to the activity $a = 1$ to the origin $Z = 0, P = 0$.

Here we use a parastatistical correction, because $N_i \leq N$, and hence the k -parastatistics holds (i.e., a parastatistics for which $N_i \leq k$) for $k \equiv N$. This allows the chemical potential μ to take very small positive values. This correction is inessential for $\gamma > 0$; however, it plays a crucial role for $\gamma < 0$ [14]. Here an important role is also played by the dimensionless quantity Λ inversely proportional to the mass of the particle.

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

Note first of all that, although N_c is large, it is still finite. Hence, we must use the parastatistical correction. Recall the relation

$$\Omega = -\Lambda^{\gamma-\gamma_c} T \sum_k \ln \left(\frac{1 - \exp \frac{\mu - \varepsilon_k}{T} N}{1 - \exp \frac{\mu - \varepsilon_k}{T}} \right) \quad (22)$$

for the Ω -potential.

Let us apply the Euler–Maclaurin formula, taking account of the parameter γ , and 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 estimate

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

and, evaluating the derivative

$$f'(x) = \frac{bk^2 e^{k(bx+\varkappa)}}{(e^{k(bx+\varkappa)} - 1)^2} - \frac{be^{bx+\varkappa}}{(e^{bx+\varkappa} - 1)^2}, \quad |R| \leq \frac{1}{\alpha} \int_0^\infty \left| \frac{k^2 e^{k(y+\varkappa)}}{(e^{k(y+\varkappa)} - 1)^2} - \frac{e^{y+\varkappa}}{(e^{y+\varkappa} - 1)^2} \right| dy^\alpha. \quad (23)$$

We also have

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

Substituting this formula into (23), 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

$$\varkappa \sim (\ln k)^{-1/4},$$

then $|R|$ has the bound

$$|R| \sim O((\ln k)^{(2-\alpha)/4}).$$

Hence, $k = N_c$ and $T = T_c$, and we obtain the following formula for the integral at $\mu = 0$:

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

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

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

We obtain (see [15])

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

Since $k \gg 1$, by setting

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

we finally obtain

$$N|_{\bar{\mu}/T=o(1)} = (\Lambda^{\gamma-\gamma_c} c(\gamma))^{1/(1+\gamma)} T, \quad \text{where } c(\gamma) = \int_0^\infty \left(\frac{1}{\xi} - \frac{1}{e^\xi - 1} \right) \xi^\gamma d\xi. \quad (24)$$

The relation

$$N = T^{\gamma_c+1} \zeta(\gamma_c + 1)$$

mates with the linear relation $N = A(\gamma)T$, where

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

for $P < 0$.

We can normalize the activity a at the point T_c . We can find a_0 by combining the liquid and gas branches at T_c for the pressure (i.e., for the quantity M) in such a way that there be no phase transition on the critical isotherm at $T = 1$.

We then further normalize the activities for $T < 1$ by using the value of a_0 evaluated below. In this case, the chemical potentials (in thermodynamics, the Gibbs thermodynamical potentials

for the liquid and gas branches) necessarily coincide, and hence there can be no phase transition “gas–liquid” at $T = 1$.

Now, for the isochor–isotherm of an “incompressible liquid” to take place, we must also construct the isochor–isotherm for a density which is less than $N_c = \zeta(\gamma_c + 1)$, namely, for

$$N(T) = T^{\gamma_c+2} \frac{|\text{Li}_{2+\gamma_c}(e^{-C/T}) - \text{Li}_{2+\gamma_c}(e^{-C/T\{1-\varepsilon(1-T_r^l)\}})|}{C}.$$

We obtain the value of $\gamma(T)$ from the implicit equation

$$A(\gamma) = T^{\gamma_c} \frac{|\text{Li}_{2+\gamma_c}(e^{-C/T}) - \text{Li}_{2+\gamma_c}(e^{-C/T\{1-\varepsilon(1-T_r^l)\}})|}{C}.$$

We thus obtain the spinodal curve, i.e., the curve of the points for which

$$\tilde{\mu} \sim T(\ln N(T))^{-1/4},$$

for $T < 1$, in the domain of negative values of γ ,

$$\Lambda^{-(\gamma-\gamma_c)/(1+\gamma)} c(\gamma)^{1/(1+\gamma)} = T^{\gamma_c} \frac{|\text{Li}_{2+\gamma_c}(e^{-C/T}) - \text{Li}_{2+\gamma_c}(e^{-C/T\{1-\varepsilon(1-T_r^l)\}})|}{C}. \quad (25)$$

We choose the least value (with the largest absolute value) of the two solutions γ of (25) and denote it by $\gamma(T)$. In particular, for $T = 1$, write $\gamma_0 = \gamma(1)$.

Let $a_g = e^{-\mu/T}$ be the activity of the gas and let $a_l = e^{-\tilde{\mu}/T}$ be the activity of the liquid. Let us present the condition that M and the activities coincide at the point of phase transition (see [26]),

$$T^{\gamma_c} \frac{|\text{Li}_{2+\gamma_c}(a_g e^{-C/T}) - \text{Li}_{2+\gamma_c}(a_g e^{-C/T\{1-\varepsilon(1-T_r^l)\}})|}{C} = \Lambda^{-|\gamma(T)|-\gamma_c} T^{-|\gamma(T)|} \text{Li}_{2-|\gamma(T)|} \left(\frac{a_l}{a_0} \right), \quad (26)$$

$$\frac{\Lambda^{\gamma_0-\gamma_c}}{\zeta(2+\gamma_0)} \text{Li}_{2+\gamma_0}(a_0) = 1, \quad (27)$$

$$a_g = \frac{a_l}{a_0}. \quad (28)$$

These two relations define the value of the chemical potential

$$\mu = \tilde{\mu} = T \ln a_g$$

at which the “gas–liquid” phase transition occurs.

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

In thermodynamics, the critical values T_c , P_c , and ρ_c were experimentally calculated for almost all gases, and hence the critical number of degrees of freedom can be prescribed in advance. The parameter Λ ($1.6 < \Lambda < 3$, $T > 1/3$) is obtained from the condition of coincidence of the binodals at the triple point, which is determined experimentally.

Remark 4. In probability theory and economics, these quantities can be determined by indirect methods only (for example, by examining the income growth rate or by studying a sufficiently large set of debt–duration pairs (duration is the period of debt repayment); see [16]). However, the

analogy with the van der Waals law of corresponding states gives hope that the scenarios of “phase transitions” must be rather similar for different states (see [17]).

In a paper by A. S. Mishchenko and the author [18], the passage to a two-dimensional Lagrangian manifold in the four-dimensional phase space is considered, where the pressure P and the temperature T (intensive variables) play the role of coordinates and the extensive variables, the volume V and the entropy S , play the role of momenta of the Lagrangian manifold, where the entropy is precisely the action generating the Lagrangian structure.

It turns out that one can carry out this complicated transformation, which leads to the Gibbs thermodynamical potential, as we have seen above, using only an extension of our considerations to the domain of negative values of γ . Then one can justify the Maxwell transition by introducing a small dissipation (a small viscosity). The introduction of infinitely small dissipation enables one to simultaneously solve the problem of critical exponents without using the scaling hypothesis, which serves as the basis for the renormalization group method. Let us show how the problem of critical exponents is solved.

There is no viscosity in thermodynamics. However, generally, a thermodynamical equilibrium cannot occur without an infinitely small dissipation. Therefore, it is natural to introduce a small viscosity and then, naturally, to assume that this small viscosity tends to zero.

The geometric quantization of the Lagrangian manifold (see [19], Subsec. 11.4) is usually associated with the introduction of the constant \hbar . One of the authors of [24] referred to the case in which the number \hbar is purely imaginary as the Wiener (or the *tunnel*) quantization [20].

Let us apply Wiener quantization to thermodynamics. The thermodynamical potential $G = \mu N$ is the action

$$\mathbb{S} = \int p dq$$

on the two-dimensional Lagrangian manifold Λ^2 in the four-dimensional phase space of the variables 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 the volume V , and p_2 is minus the entropy S . All other potentials, i.e., the internal energy E , the free energy F , and the enthalpy W are the results of projection of the Lagrangian manifolds to the coordinate planes p_1, p_2 ,

$$\begin{aligned} E &= - \int \vec{q} d\vec{p}, \quad \vec{q} = \{q_1, q_2\}, \vec{p} = \{p_1, p_2\}, \\ W &= - \int (q_2 dp_2 + q_1 dp_1), \quad F = \int (q_1 dp_1 - q_2 dp_2). \end{aligned} \tag{29}$$

Under Wiener quantization, we have

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

Hence the role of time t in the quantization is played by $\ln(-\mu/T)$,

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

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

As we shall see below, the critical point and the spinodal points are focal points, and hence do not pass into “classics,” i.e., to the vdW model, as $\varepsilon \rightarrow 0$. The spinodal points, like the turning points in quantum mechanics, are approximated by the Airy function, and the critical point, which

is the point at which two turning points (two Airy functions) occur, is approximated by the Weber function (see [21]). The point of creation of a shock wave in the Burgers equation is expressed in terms of the Weber function itself as $\varepsilon \rightarrow 0$. If the passage to the limit as $\varepsilon \rightarrow 0$ is carried out outside these points, then the vdW–Maxwell model is obtained. However, the passage to the limit is violated at these very points by themselves. Therefore, it turns out that the so-called “classical” critical Landau exponents [3] disagree with experiments seriously. The Weber function gives singularities of the form $\varepsilon^{-1/4}$, and the Airy function gives a singularity of the form $\varepsilon^{-1/6}$.

Let us now consider the Burgers equation in more detail.

Consider the heat equation

$$\frac{\partial u}{\partial t} = \frac{\varepsilon}{2} \frac{\partial^2 u}{\partial x^2}, \quad zx \in \mathbb{R}, \quad t \geq 0, \quad (30)$$

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

$$u = \lambda_1 u_1 + \lambda_2 u_2 \quad (31)$$

of solutions u_1 and u_2 to (30) are also solutions of this equation.

Let us make the change of the variable

$$u = \exp(-w(x, t)/\varepsilon). \quad (32)$$

We obtain the following nonlinear equation:

$$\frac{\partial w}{\partial t} + \frac{1}{2} \left(\frac{\partial w}{\partial x} \right)^2 - \frac{\varepsilon}{2} \frac{\partial^2 w}{\partial x^2} = 0, \quad (33)$$

which is referred to as the integrated Burgers equation⁵.

Obviously, to any solution u_i of equation (30), one can assign the solution $w_i = -\varepsilon \ln u_i$ of equation (33), $i = 1, 2$. To the solution (31) of equation (30), one can assign a solution of equation (33), $w = -\varepsilon \ln \left(e^{-\frac{w_1 + \mu_1}{\varepsilon}} + e^{-\frac{w_2 + \mu_2}{\varepsilon}} \right)$, where $\mu_i = -\varepsilon \ln \lambda_i$ ($i = 1, 2$). Since

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

we obtain the $(\min, +)$ algebra of tropical mathematics [22].

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

$$\frac{\partial v}{\partial t} + v \frac{\partial v}{\partial x} - \frac{\varepsilon}{2} \frac{\partial^2 v}{\partial x^2} = 0, \quad v|_{t=0} = p_0(x), \quad (34)$$

and to refer to the function

$$p_{\text{ge}} = \lim_{\varepsilon \rightarrow 0} v$$

(Riemann waves) as a (generalized) solution to the equation

$$\frac{\partial p}{\partial t} + p \frac{\partial p}{\partial x} = 0, \quad p|_{t=0} = p_0(x). \quad (35)$$

⁵The usual Burgers can be derived from equation (33) by differentiating with respect to x and making the change $v = \partial w / \partial x$.

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

$$v = -\varepsilon \frac{\partial}{\partial x} \ln u \tag{36}$$

of a solution u of the heat equation

$$\frac{\partial u}{\partial t} = \frac{\varepsilon}{2} \frac{\partial^2 u}{\partial x^2}, \quad u|_{t=0} = \exp \left\{ -\frac{1}{\varepsilon} \int_{-\infty}^x p_0(x) dx \right\}. \tag{37}$$

Thus, the initial problem is reduced to studying the logarithmic limit of the solution of the heat equation. As is known, the solution of problem (37) is of the form

$$u = (2\pi\varepsilon t)^{-1/2} \int_{-\infty}^{\infty} \exp \left\{ -((x - \xi)^2 + 2t \int_{-\infty}^{\xi} p_0(\xi) d\xi) / 2th \right\} d\xi. \tag{38}$$

The asymptotic behavior of the integral (38) can be found by using the Laplace approach. For $t < t_{cr}$, we have

$$u = (|J|^{-1/2}(\xi(x, t), t) + O(\varepsilon)) \exp \left\{ -\frac{1}{\varepsilon} S(x, t) \right\}. \tag{39}$$

Here

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

the integral is calculated along the Lagrangian curve Λ^t , and the point $r(x)$ belongs to Λ^t . For $t > t_{cr}$, there are three points $r_1(x), r_2(x), r_3(x)$ on Λ^t whose projections to the axis x coincide or, 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

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

$$S(x, t) = \min(S_1, S_2, S_3). \quad S_j = \int_{-\infty}^{r_j(x)} p dx,$$

where $j = 1, 2, 3$ for $x \in [x_1, x_2]$.

The above considerations enable one to obtain a generalized discontinuous solution of problem (35) for times $t > t_{cr}$. It is given by the function $p = p(x, t)$ determining essential domains [20] of the curve Λ^t . Note that, in particular, this implies the rule of equal areas known in hydrodynamics to define the front of the shock wave whose evolution is described by equation (35). We note that this exactly 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 calculated by the formula

$$v(x, \varepsilon) = \varepsilon \frac{\partial \ln u(x)}{\partial x} = \frac{\int_0^{\infty} \exp\left\{ \frac{-x\xi - \xi^4/4}{\varepsilon} \right\} \xi d\xi}{\int_0^{\infty} \exp\left\{ \frac{-x\xi - \xi^4/4}{\varepsilon} \right\} d\xi}. \tag{40}$$

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

$$v(\varepsilon, x) \rightarrow_{x \rightarrow 0} \sqrt[4]{\varepsilon} \cdot \text{const.} \tag{41}$$

What does this mean from the point of view of classics and classical measurements, i.e., for the case in which the so-called ‘‘semiclassical’’ condition holds (in the terminology used in the book [23])

(i.e., for the case in which we are outside the focal point)? For the Laplace transformation, this means that we are in the domain where the Laplace asymptotic method can be applied, i.e., where

$$u(x) = \frac{1}{\sqrt{\varepsilon}} \int_0^\infty e^{-\frac{px - \tilde{S}(p)}{\varepsilon}} dp. \quad (42)$$

Moreover, the solution of the equation

$$x = \frac{\partial \tilde{S}}{\partial p} \quad (43)$$

is nondegenerate, i.e., $\frac{\partial^2 \tilde{S}}{\partial p^2} \neq 0$ at the point $\frac{\partial \tilde{S}}{\partial p} = x$, and, in this case, the reduced integral (42) is bounded as $\varepsilon \rightarrow 0$. For this integral to have a zero of order $\varepsilon^{1/4}$, we must integrate the integral with respect to x by the fractional derivative $D^{-1/4}$. The value of $D^{-1/4}$ as applied to one, $D^{-1/4}1$, gives approximately $x^{1/4}$.

By the indeterminacy principle [24], the correspondence between the differentiation operator and a small parameter of the form $D \rightarrow 1/\varepsilon$ is preserved for the ratio $-\varepsilon \frac{\partial u / \partial x}{u}$, although the leading term of the asymptotic expansion for the difference between $\frac{\partial^2 u / \partial x^2}{u}$ and $\frac{(\partial u / \partial x)^2}{u^2}$ is cancelled.

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

$$P_c \sim (V - V_c)^4. \quad (44)$$

This is precisely the jump of the critical exponent. The other critical exponents can be obtained in a similar way [24]. The comparison with experimental data is discussed in the same paper.

Remark 5 For $\gamma = 1/2$, one can say that a normal 3-dimensional Bose gas is considered. In this case, the volume and the reflection from the boundary is called a trap.

* * *

In conclusion, let us sum up the above considerations.

The vapor–liquid equilibrium is achieved if an infinitesimal dissipation is introduced, i.e., a dissipation introduced to play a role in establishing the equilibrium state, and then this dissipation tends to zero.

After establishing such an equilibrium by using quantization and by passing to the limit as the quantization parameter tends to zero, pure number theory comes into play. Below the critical temperature, equilibrium occurs at $N = N_c$, i.e., the further growth of the number of gas particles eventually leads to their fall into the Bose condensate.

When reducing the volume of gas (vapor), the number of particles becomes greater than N_c , and the excessive particles, passing into the liquid in the case of the above equilibrium, fall further to the Bose condensate.

Although all experts stress the analogy between Bose condensate and saturated vapor, the fact that this is a direct mathematical consequence of the effect of adding zeros to the problem of “partitio numerorum” in number theory⁶ causes the same reaction of most theoretical physicists, of the type “This is impossible!” (see [25]).

⁶Adding of zeros to “partitio numerorum” is unusual for mathematicians which are experts in the number theory either. I could not explain this passage to Academician I. R. Shafarevich, a world-known expert in number theory, who responded to this insolence (the introduction of zeros to the classic problem of “partitio numerorum”) in an interview to V. B. Demidovich: “... Among these “obscure” mathematicians, I remember the Nikolai Nikolaevich Bogolyubov, now deceased. I also refer Victor Pavlovich Maslov, now alive, to the same group. I absolutely could not understand him; he says an obviously incorrect phrase and, until you understand that it is wrong and construct a counterexample, he is already saying something else, and you lag permanently behind him.”

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