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New Critical Points for the Liquid Phase and the Construction of Thermodynamics Depending on the Interaction Potential[*]

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Abstract—The author constructs a one-particle distribution generalizing the Maxwell—Boltzmann and Bose—Einstein distributions for classical particles, without incurring the Gibbs paradox, and, simultaneously, constructs the thermodynamics of fluids and phase transitions on the basis of the concept of creation of dimers and clusters and obtains well-known laws and relations of thermodynamics as well as explains some recently, discovered effects (such as the jamming effect).

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1. ON THE NEW CRITICAL POINT FOR THE LIQUID PHASE

Earlier we have explained the jamming effect (i.e., that of incompressibility of fluids) by using a new distribution close to the Bose—Einstein distribution. Further, using a scheme for finding the distance between rest points in the scattering problem, we found the Zeno line and the critical points T_{cr}, Z_{cr}, and ρ_{cr}. In this section, we wish to show that there exists another critical point in the liquid phase; it is also related to the jamming effect, which, as is known, is related to vitrification. The process of conversion of liquid into glass proceeds smoothly, with no aerosols and admixtures in the liquid phase and without a phase transition of the first kind of liquid to crystal.

This effect was not obtained for noble gases for which the results of our previous calculations of the critical constants and of the binodal were in best agreement with experimental data. However, such vitrification was carried out for some other substances, including water and solutions [1].

Ginzburg with his colleagues actively studied this problem. They studied hydrogen, trying to preserve liquid hydrogen in order to observe superfluidity. We can state that, at present, quite a few physicists do not doubt that there must exist a critical point in the liquid phase (and, in He4, such a point is the λ-point).

In this section, we determine such a critical point, a hypothetical λ-point for a liquid which was not discovered experimentally. Nevertheless, the presence of a λ-point significantly supplements the pattern of the distribution that was constructed by the author for a classical gas.

The hypothetical λ-point in the liquid domain cannot be discovered experimentally because of the transition to crystal. But if we could preserve the metastable state liquid—glass, then it would arise for $Z \sim 0$. Let us show this on the diagram (Fig. 1), using the Bose—Einstein distribution with the author's correction

$$\Omega^{\mathrm{id}}_{\gamma} = \frac{\pi^{1+\gamma}T^{\gamma+2}V}{\Gamma(\gamma+2)}\int_0^{\infty}\xi^{1+\gamma}\biggl\{\frac{1}{e^{(\xi-\kappa)}-1}-\frac{N}{e^{(\xi-\kappa)N}-1}\biggr\}d\xi, \qquad \kappa=\frac{\mu_{\gamma}}{T}, \tag{1}$$

where $\Gamma(\cdot)$ is the gamma function (cf. [1]).

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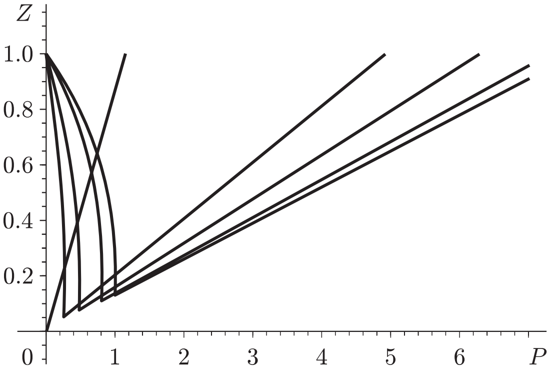

Fig. 1. Isotherms in the liquid phase domain. The hypothetical λ-point in the liquid phase corresponds to $Z \sim 0$, $P \sim 0$. For $Z = 1$, the lines run into the Zeno line.

In the two-dimensional case, for the unit volume, it is natural to normalize T by the ratio P/N for $\mu = -\infty$ and pass to the two-dimensional Maxwell distribution

$$N = \lim_{\mu=-\infty} e^{\mu/T} \int \frac{p\,dp}{e^{(p^2/2mT)-(\mu/T)} - 1}\,, \tag{2}$$

$$P = \lim_{\mu=-\infty} e^{\mu/T} \frac{1}{2m} \int \frac{p^3\,dp}{e^{(p^2/2mT)-(\mu/T)} - 1}\,. \tag{3}$$

The temperature $T_0 = P/N$ is taken as the unit, and we set

$$T_r = \frac{T}{T_0}.$$

Since [2], [3] we have

$$N_{cr} = \frac{1}{\beta} \ln N_{cr}; \tag{4}$$

in view of (2), (3),

$$T_0 \sim \sqrt{N}, \qquad \frac{T_{cr}}{T_0} \sim \ln N_{cr}, \qquad \mu = T - T_{cr}$$

in the formula for N and

$$c_p \cong \frac{2T}{T_0} \int_0^\infty \frac{\xi\,d\xi}{e^\xi - 1} + \frac{T}{T_0} \int_0^\infty \frac{e^\xi \xi\,d\xi}{(e^{\xi-\mu/T} - 1)^2} + O\biggl(\frac{T - T_{cr}}{T_0}\biggr). \tag{5}$$

Thus, because μ also takes small positive values [4], a metastable λ-point arises if the phase transition to crystal can be prevented.

By Bose–Einstein theory, the isotherms shown in Fig. 1 follow from the following formulas for $\gamma = 0.2$ ($Z_{cr} = 0.29$). Suppose that $T = \text{const}$, $d\mu = V_r dP_r$, $V_r = V/V_{cr}$ is the volume, $P_r = P/P_{cr}$ is the pressure, and μ is the dimensionless chemical potential.

Denote

$$y = e^\mu, \qquad 0 \ge \mu > -\infty,$$

as $\mu \to -\infty$ and $y \to 0$.

Then, for an ideal Bose gas,

$$Z(y) = \frac{\Gamma(\gamma+1)}{\Gamma(\gamma+2)} \frac{\displaystyle\int_0^\infty \frac{\varepsilon^{\gamma+1}\,d\varepsilon}{e^\varepsilon - y}}{\displaystyle\int_0^\infty \frac{\varepsilon^\gamma\,d\varepsilon}{e^\varepsilon - y}}\,.$$

Therefore,

$$d\mu = d\ln\, y = V_r dP_r = T_r Z(y) d\ln\, P_r, \tag{6}$$

and hence

$$\frac{d\ln\, y}{Z(y)} = T_r d\ln\, P_r, \qquad y = y(P_r^{T_r}).$$

The angle of inclination of the lines $T = \text{const}$ to the line $Z = 1$ is known; it is

$$\frac{dT}{dP} = \frac{\rho}{\rho_B}\biggl(1 - \frac{2T}{T_B}\biggr).$$

The points T are also determined on $Z = 1$ [5]. They correspond to the points ρ that are constant (to our degree of accuracy) up to the minimal Z. We see that, up to rotation (i.e., the change $V \to \varphi_\gamma(V)$ in the Bose–Einstein distribution), the pressure is not constant with respect to the transition gas–liquid, although it varies not significantly along the almost-horizontal parts of the isotherms.

However, we can determine the hyperbola responsible for the jamming effect for the liquid phase if $Z < 0.17$ (see [6]):

$$\frac{\rho}{\rho_B}\biggl(1 - \frac{\rho}{\rho_B}\biggr) = \frac{T}{T_B}\biggl(1 - \frac{T}{T_B}\biggr). \tag{7}$$

This curve must be plotted on the ρ, T diagram. It corresponds to the almost-incompressibility of the liquid as the pressure increases.

Since the point T_1 is fixed on the line $Z = 1$, it follows that, on the Z, P diagram, it corresponds to the point P_1. On the line $Z = 1$, there exists another point equal to T_1 which corresponds to another value of P_1'. The closer T is to zero, the closer P_1' is to zero as well.

Finding the value of P_1', we plot it on the abscissa. This is the endpoint of the inclined isotherms and, accordingly, at this point, we know Z_1 in the liquid phase.

Thus, for $Z \le 0.17$, in the liquid phase, we completely determine the dependence $Z(T)$, $P(T)$, and $\rho(T)$ up to the hypothetical λ-point.

2. CONSTRUCTION OF THE BINODALS

In thermodynamics, experiments do not always provide unequivocal answers. Old experiments were carried out in the earth's gravitational field. The divergences in the experimental determination of the so-called Boyle point (the Boyle temperature) are very large.

The main problem is to determine whether the pressure is the same in a two-phase liquid in vapor–liquid equilibrium. As a rule, a small drop of liquid is put in a vessel so that the pressure of the vapor is several times less than that of saturated vapor. The drop evaporates and becomes smaller until equilibrium is established. However, the additional pressure created by surface tension is not taken into account.

Conversely, in order to determine the critical point, studies are conducted in a test tube and concern a wettable liquid whose meniscus is concave and whose pressure near the critical point is less than that of the vapor. If the liquid drops are small and there is no gravitational pull, then they form one large drop so as to maximize the entropy. This is possible only because there is Brownian motion of the droplets.

Essentially, we deal with “noise” in all our arguments concerning a trap for a dimer, because a classical particle reaching the maximum of the barrier in infinite time must stop there if neither the quantum effect nor the effect of the noise is taken into account.

We neglect the quantum effect, because the de Boer parameter equal to $h/a\sqrt{2\pi m\varepsilon}$, where a is the effective radius of the molecule and ε is the depth of the potential well in the interaction potential, is sufficiently small for classical gases.

Therefore, only the noise effect remains.

It turns out that we can draw a complete analogy between the noise intensity parameter $D = 2\Gamma T$, where Γ is the friction coefficient and T is the temperature for the unit mass, and the coefficient $h^2/2$

in the Schrödinger equation. In the theory of the instanton and penetration through the barrier, the formulas first obtained by the author [7], [8],[1] [9] and the formulas for the instanton in the survey [10] are totally identical.

In the construction in which we define the critical temperature, we consider the difference of the energies of the stable and unstable rest points. Furthermore, we use only small friction and viscosity. Indeed, as a result of small viscosity, a classical particle, after having flown "just" above the barrier, will lose its energy and, on reflection, will hit the barrier and will continue hitting the walls of the barrier and the walls of the potential in the form of a well until it precipitates to the bottom. (The value of the energy of the stable rest point is E_1 and the value of the energy of the unstable rest point E_2.) To knock out this particle from the well trap, the required kinetic energy must be "slightly" greater than the difference between the energies $E_1 - E_2$ of the rest points. This can interpreted as a break-up of the dimer in the collision with a fast monomer. The equilibrium is violated when the depth $E_1 - E_2$ of the well decreases and its width increases as the absolute value of the energy E_1 of the stable rest point decreases (as the impact parameter increases). It is natural to regard the increasing width as a result of an increase in the numbers of dimers in the trap (in quantum theory, this corresponds to an increase in spectral density). Dimers clusters can survive and equilibrium between the monomers and the dimers can be preserved only if the dimers themselves combine into cluster domains and create their own barrier, which is a microanalog of a surface film.

How about the pressure in this natural interpretation and the fact that the theoretical values of the critical temperature are in good agreement with the corresponding experimental data?

In the scattering problem, the interaction potential is taken as the Lennard-Jones potential

$$\Phi(r_1, r_2) = 4\varepsilon\biggl(\frac{a^{12}}{\|r_1 - r_2\|^{12}} - \frac{a^6}{\|r_1 - r_2\|^6}\biggr), \tag{8}$$

where ε is the energy of the well depth, a is the effective radius, and $\|r_1 - r_2\|$ is the distance between two particles with radius vectors r_1 and r_2. In the two-particle problem, the problem reduces to a one-dimensional radially-symmetric problem if there is no external potential.

We consider the two-body problem in which the energy E and the moment M are related by the relation

$$E = \frac{mv^2}{2} + \frac{M^2}{2mr^2} + \Phi(r), \qquad v = \frac{dr}{dt}\,, \tag{9}$$

where $r = r_1 - r_2$, $m = m_{1,2}/2$, and $m_1 = m_2$ are, respectively, the coordinates and masses of each of the two particles, the origin is at the center of inertia, and t is the time.

To relate the problem of finite motion to the scattering problem, we introduce an impact parameter B in the finite-motion problem. As is well known,

$$\frac{M^2}{2m} = B^2 E. \tag{10}$$

Now the total energy E is related to the impact parameter B by the following important formula:

$$E = \frac{(mv^2)/2 + \Phi(r)}{1 - B^2/r^2} \tag{11}$$

in the domain $a < r \le B$, where a is the effective radius of the Lennard-Jones potential.

In this formula related to the scattering problem, the total energy is equal to the kinetic energy of the hypothetical particle falling with velocity v. The kinetic energy $mv^2/2$ defines the temperature as well.

The greater is the kinetic energy $mv^2/2$, the less is the total energy of the finite motion in view of the negative term

$$\frac{mv^2/2}{1 - B^2/r^2}\,.$$

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[1] This paper was presented on my behalf by S. Yu. Dobrokhotov at the International Conference on Analytic Methods in Number Theory and Analysis (Moscow, September 14–19, 1981), because I was ill at that time.

In problem (11), different barriers and wells occur for different values of B. At the rest points, $E_{\min}$ and $E_{\max}$, the velocity is zero; therefore, they can be determined only from the potential term.

We are now dealing not with just one particle, but with a pair of particles whose mass center is in the trap. Therefore, the difference $E_{\max} - E_{\min}$ is the energy needed to knock out this pair (the dimer) from the trap.

Experimentally, we can calculate the percentage of dimers in a gas. It is clear how dimers are created and split by monomers. Further, their mean number is calculated. The higher is the temperature, the greater is the mean energy of monomers and the smaller the number of dimers.

By our calculations, we have $T_{cr}/T_B = 2.79$. According to the contemporary handbooks, this value is $T_{cr}/T_B = 2.72$ for argon (Ar), $T_{cr}/T_B = 2.71$ for krypton (Kr), $T_{cr}/T_B = 3.157$ for methane (CH_4), and $T_{cr}/T_B = 2.6$ for nitrogen (N_2). (Other data is given in [11].)

In Table 1, comparative data for $T_{cr}/4$ are given.

Table

Substance	ε, K	$T_{cr}/4$	$E_{cr} \cdot \varepsilon/k$
Ne	36.3	11	10.5
Ar	119.3	37	35
Kr	171	52	50
N_2	95, 9	31	28
CH_4	148.2	47	43
C_2H_6	243.0	76	70

As is well known, if we take small friction Γ into account, then diffusion or noise intensity is of the form $D = 2\Gamma T$ for the unit mass. According to the classical papers of Pontryagin, Andronov, and Vitt (see [12]), an increase in noise intensity entails an increase in the probability of a jump over the barrier, i.e., which is equivalent to the apparent lowering of the barrier. Is this not the reason for the deviation to one side of the theoretical values of temperatures from the experimental ones?

Let us now pass to a more detailed study of the Z, ρ diagram. The scattering problem for the Lennard-Jones potential does not involve the volume.

Since, as is well known, Z begins on the (ρ, T) binodal, we can use the dependence (given above) up to $Z = 0.444$ and then include the thermic potential, because we must also take into account the influence of a third particle. As was already stated in previous papers, the dressed, or "thermic," potential $\Psi(r)$ is attractive. In addition, since the volume V is a large parameter, it follows that if

$$\Psi(r) = \Psi\left(\frac{ar^2}{V}\right),$$

where a is the effective radius, we can expand in terms of $1/V$, obtaining

$$\Psi\left(\frac{ar^2}{V}\right) = C_1 + \frac{C_2 ar^2}{V} + O\left(\frac{1}{V^2}\right). \tag{12}$$

Expanding

$$r^2 = r_1^2 + r_2^2 = \frac{(r_1 - r_2)^2}{2} + \frac{(r_1 + r_2)^2}{2}, \tag{13}$$

we can, just as in [13], separate the variables in the two-particle problem and obtain two separate scattering problems, one for a pair of particles and one for their joint (for $r_1 + r_2$) motion.

Then, in the scattering problem, the Lennard-Jones interaction potential is supplemented by a quadratic potential (an inverted parabola), i.e.,

$$E = \frac{mv^2/2 + \Phi(r) - C_2 ar^2/2V}{1 - B^2/r^2}. \tag{14}$$

In the range of $Z = 0.444$ to $Z_{cr} = 2/3 \cdot 0.444$, we use a hyperbola[2] and, below $Z = 0.17$, as stated above, significant changes begin: the liquid becomes practically incompressible and the hyperbola (7) is used.

The curve $1 - Z_{\min}(\rho)$ on the Z, ρ diagram takes the form shown in Fig. 2.

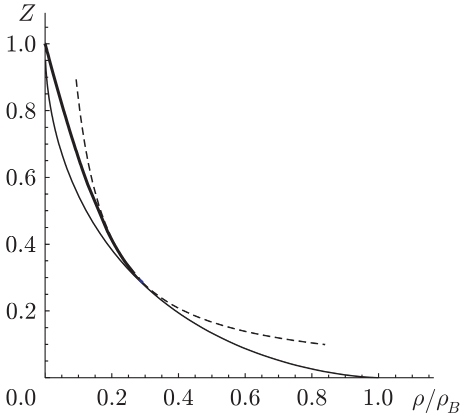

Fig. 2. The curve $Z(\rho)$ from the point $Z = 0.17$ to the point $Z_{cr} = 0.29$ coincides with the thin curve and further with the thick one. The dotted line denotes the hyperbola joining the problem without thermic potential (11) with the problem with thermic potential (14).

The curve $1 - Z_{\min}$ on the (Z, ρ) diagram can be calculated by using the Zeno line. As was already stated, for $Z \geq 0.444$, the dimension $d = 2.8$ $(\gamma = 0.4)$ does not change. Therefore, by our general concept, the distribution under consideration is a number-theoretic distribution up to the critical point, i.e., up to the creation of dimers; for $d = 2.8$ $(\gamma = 0.4)$, our distribution coincides with the Bose—Einstein distribution, in which the number-theoretic distribution is multiplied by the volume V. But, in our distribution, the multiplier is a function of V, i.e., we have the following replacement of the multiplier in the Bose—Einstein distribution:

$$V \to \varphi_\gamma(V).$$

The index γ is sometimes dropped, because it is constant here. This function is constant for this dimension. Therefore, $Z_{\min}$ obtained for $\mu = 0$ is of the form

$$Z_{\min} = \frac{\varphi'_\gamma(V)}{\varphi_\gamma(V)} \cdot \frac{\zeta(d+1)}{\zeta(d)}, \tag{15}$$

where ζ is the Riemann zeta function and $\gamma = 0.4$.

For any $Z \leq 1$, we have

$$Z = \frac{\varphi'_\gamma(V)}{\varphi_\gamma(V)} \cdot \frac{\Gamma(\gamma+1)}{\Gamma(\gamma+2)} \cdot \frac{\displaystyle\int_0^\infty \frac{\varepsilon^{\gamma+1}\,d\varepsilon}{e^{\xi-\kappa}-1}}{\displaystyle\int_0^\infty \frac{\varepsilon^{\gamma}\,d\varepsilon}{e^{\xi-\kappa}-1}} = \frac{\varphi'_\gamma(V)}{\varphi_\gamma(V)}\Psi(\kappa), \qquad \kappa = \frac{\mu}{T}, \quad \varphi'_\gamma(V) = \frac{\partial\varphi}{\partial V}, \tag{16}$$

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[2] On this large interval, there is a very small variation of the temperature and pressure with respect to Z and the volume V. Thus, for argon, the temperature varies $147 - -151°$ K and the pressure in the range $42 - -49$ atm.

where $\Gamma(\cdot)$ is the gamma function. For $\kappa = 0$, we obtain (15). Further, we obtain $\mu(T, V)$ as a function of V from the condition

$$\frac{\varphi_\gamma'(V)}{\varphi_\gamma(V)}\Psi(\kappa) = 1, \qquad \kappa = \kappa(V).$$

On the other hand, for $Z = 1$, we have the Bachinskii parabola following from the slope of the Zeno line. Therefore, the dependences $P(T)$, $T(\rho)$, $P(\rho)$ are well known: $P(T)$ is the Bachinskii parabola, $T(\rho)$ is a hyperbola, and $P(\rho)$ is a parabola.

Let us find P from the modified Bose–Einstein distribution

$$P = \frac{\varphi_\gamma'(V)T^{\gamma+2}}{\Gamma(\gamma+2)}\int_0^\infty \frac{\varepsilon^{\gamma+1}\,d\varepsilon}{e^{-\kappa}e^{\varepsilon}-1}, \tag{17}$$

where the value $\kappa = \kappa(V)$ is expressed in (16) in terms of $\varphi_\gamma(V)$ and $\varphi_\gamma'(V)$. Hence, from the Bachinskii parabola $P(\rho)$ ($\rho = 1/V$), we uniquely obtain an ordinary differential equation of first order for the function $\varphi(V)$. The constant is determined from the condition $\varphi(V)/V \to 1$ as $V \to \infty$ (transition to the ideal gas; cf. [5]).

The value of the functions $\varphi_\gamma(V)$ were obtained above for $Z \le 0.17$. The value of the function $\varphi(V)$ on the hyperbola $Z = \rho_{cr}/\rho$ was calculated in [5]. The interval ($Z = 0.17$, $Z = 0.29$) contains a new variable parameter $\gamma \le 0.2$. Now the function $\varphi_\gamma(V)$ also depends on γ. Therefore, using two conditions on $Z_{\min}$ (the interval of the thin curve and the value of $\varphi_\gamma(V)$ for $Z = 1$) and the same dependences on $Z = 1$ that were mentioned above, we can determine the isotherms (this was done approximately in [5, Fig. 5]). From the value of $Z_{\min}(\rho)$ on the thin curve (for the impact parameter $B \gg 1$), we obtain

$$\frac{\varphi_\gamma'(V)}{\varphi_\gamma(V)}\Psi_\gamma(0) = Z_{\min}\left(\frac{1}{V}\right).$$

Therefore, we must now find $\kappa(V, \gamma)$ from the condition $Z = 1$:

$$\Psi_\gamma(\kappa) = \frac{\Psi_\gamma(0)}{Z_{\min}\left(\frac{1}{V}\right)}\,.$$

Using condition (17), as well as the substitution of $T(\rho)$ and $P(\rho)$, we can determine the expression for $\gamma(\rho)$ from the implicit equation. On the line $Z = 1$, two different values of ρ, ρ_{gas} and ρ_{liquid}, yield two different values of $\gamma(\rho)$. For $Z = 1$, it is convenient to express all quantities in terms of the temperature according to the hyperbola $T(\rho)$. In this case, T_{cr} and P_{cr} play a role.

Thus, it turns out that, in addition to the calculation of the Zeno line, the most important interval of the curve $1 - Z_{\min}$ is the interval from $Z = 0.29$ to $Z = 0.17$. Only using this interval, we can find the function $\varphi_\gamma(V)$, which is needed to describe the one-particle distribution with respect to p and q for the case of the Lennard-Jones interaction.

As was already stated by the author, the equations of state are equations of the two-dimensional surface Λ^2 in four-dimensional phase space, where the role of the coordinates x, y is played by the intensive quantities P, T (pressure and temperature) and the role of momenta p_x, p_y is played by the quantities V and $-S$ (V is the volume and S is the entropy).

In the coordinate plane, it is natural to transform to polar coordinates $r = \sqrt{x^2+y^2}$ (radius vector) and $\arctan(x/y)$ (angle); namely, we set

$$\varphi = \arctan\frac{PT_{cr}}{P_{cr}T}.$$

On the ($0 \le \varphi \le 2\pi$, ρ) diagram, we can construct the φ, ρ-binodal in which with each φ we associate the jump $\rho_{gas} \to \rho_{liquid}$. In the same way, we can construct the φ, Z-binodal. If the temperature in both phases is the same, then the φ, ρ-binodal implies that the values of the pressure in both phases are equal.

As was already stated, the curve $1 - Z_{\min}$ must be supplemented with the hyperbola (7) for $Z \le 0.17$.

The subtraction process from the oblique line joining the endpoints of the curve (7) yields the T, ρ-binodal if the dimensionless quantities Z are replaced by T/T_B. However, the resulting curve must be orthonormalized so that the maximum of the binodal coincides with the value of T_{cr}/T_B. This subtraction process is a result of the construction of wells corresponding to different values of B, because the wells terminate on the curves, where $E_{\min} = E_{\max}$, i.e., on the Zeno line.

For $Z > 0.17$, the values of the pressure in the two phases on the resulting T, ρ-binodal will differ insignificantly.

Thus, the construction of a distribution generalizing the one-particle Maxwell–Boltzmann distribution and the Bose–Einstein distribution, is closely related to the construction scheme for a binodal and a Zeno line.

Of course, if the thermodynamics of a particular gas is known, then, as was already stated, we can uniquely construct this distribution. It is interesting, however, to solve both problems together by using a scheme involving rest points and the creation of dimers and clusters, instead of the fall of particles to the lower level and the construction of the multiplier $\varphi_\gamma(V)$ for a number-theoretic distribution.

The author called the two-dimensional surface Λ^2 the *Lagrangian manifold* [14] and introduced the notion of *tunnel canonical operator* [15] (see also [16]), where, for the large parameter $1/h$, one must take $1/\sqrt{D}$, where D is the diffusion or noise intensity. The higher is the temperature, the greater is the degree of departure from the standard thermodynamics and from the phase transition gas–liquid. caused by the tunnel canonical operator.

For such a transition, the temperature remains constant, while the pressure and the values of the volumes are somewhat changed. As was already stated, this is especially noticeable at the focal point under the rotation of $T = T_{cr}$ with respect to the compressibility factor Z.

Remark. The inclusion of the thermic potential in the original problem is equivalent to bringing in at least one other (third) particle. Obviously, the value $Z_{\min}(\rho)$ or $Z = 1 - Z_{\min}(\rho)$ ($Z_{\max} < 1$) must be affected by the inclusion of a third particle, while we consider the interaction of two particles. If, in the study of two particles, we include the thermic potential as an external one, then we must ensure, in our problem, at least maximal repulsion of two particles from each other by making them collide head-on. Then we can hope that the attraction provided by the thermic potential will guarantee the maximum value of $Z = 1 - Z_{\min}(\rho)$. But such a transition from a two-particle problem to the introduction of a thermic potential must preserve "consistency."

Addition to a two-particle problem of friction related to the chaos of a gas and, further, of a thermic potential provide simple and natural conditions related to our *a priori* knowledge. It is not known beforehand to what degree these elementary considerations are consistent with the complex laws of thermodynamics.

3. CONCLUSIONS

In this paper, we have discussed two new smoothed phase transitions.[3] The first smoothed transition is called a *smoothed transition of the "first kind"*; it occurs in the interval from $Z = 0.444$ to $Z_{cr} = 2/3 \cdot 0.444 = 0.296$ and is a cascade transition of dimers to clusters observed in superfluid flows [17], etc. It is smoothed by gas diffusion, i.e., by the tunnel canonical operator, where, instead of the parameter h, we have the parameter $\sqrt{D}$, where D is the noise intensity. For the (ρ, T) diagram, we deal with a hyperbolic transition, while, for the (Z, P) diagram, we have a smoothed jump of Z and V.

The second smoothed transition is called a *Zeno transition*; it is a transition to the state of the hypothetical λ-point for $Z \le 0.17$. This is the hyperbolic transition in the (T, ρ) diagram (and the oblique line in the $(P, 1/T)$ diagram). For each value of T and constant volume, the dimension, as P increases, tends to 2, but does not attain the value 2 (i.e., the λ-point). For $Z = 0$, there appears a hypothetical λ-point.

Initially, we consider these transitions as step-wise (i.e., phase) transitions, but the tunnel canonical operator smoothes them so that they become smoothed transitions. The tunnel canonical operator hardly smoothes ordinary phase transitions of the first kind at low temperature: in such a transition, the temperature remains constant and the pressure and density change slightly.

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[3] Similar to smoothed ionization.

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