Can a crystal be the ground state of a Bose system?

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It is usually assumed that the Bose crystal at $T = 0$ corresponds to the genuine ground state of a Bose system, i.e., this state is non-degenerate and is described by the wave function without nodes. By means of symmetry analysis we show that the ground state of a Bose system of any density should correspond to a liquid or gas, but not to a crystal. The main point is that any anisotropic state of a system of spinless bosons is degenerate. We prove this for an infinite three-dimensional (3D) system and a finite ball-shaped 3D system. One can expect that it is true also for a finite system of any form. Therefore, the anisotropic state cannot be the genuine ground state. Hence, a zero-temperature natural 3D crystal should correspond to an excited state of a Bose system. The wave function $\Psi^c_0$ of a zero-temperature 3D Bose crystal is proposed for zero boundary conditions. Apparently, such $\Psi^c_0$ corresponds to a local minimum of energy (absolute minimum corresponds to a liquid). Those properties yield the possibility of existence of superfluid liquid $\text{H}_2$, Ne, Ar, and other inert elements. We propose several possible experimental ways of obtaining them.

Keywords: Bose crystal; ground state; degeneracy; superfluidity.

1 Introduction

In the Nature, liquids usually crystallize at the cooling. This leads to the natural commonly accepted assumption that the lowest state of a dense three-dimensional (3D) Bose system corresponds to a crystal. However, we will see in what follows that this is apparently not the case. The question about the structure of the ground state (GS) is of primary importance. In a strange way, it has been little investigated in the literature. Below, we will try to clarify this question mathematically (Sect. 2) and consider the possible experimental consequences (Sect. 3). In this regard, we mention the book by K. Mendelsohn, that provides an excellent review of the history of the development of low-temperature physics till 1965.
2 Mathematical substantiation

2.1 Ansätze for the wave function of the ground state of a Bose crystal

Consider \( N \) spinless interacting bosons without any external field. The Hamiltonian of such a system reads

\[
\hat{H} = -\frac{\hbar^2}{2m} \sum_{j=1}^{N} \Delta r_j + \frac{1}{2} \sum_{j \neq j'} U(|r_j - r_{j'}|). \tag{1}
\]

In the literature, three solutions were proposed for the GS wave function (WF) \( \Psi_0^c \) of a Bose crystal. All of them correspond to WF without nodes. Thus, it was assumed that the crystal at \( T = 0 \) corresponds to the genuine GS of the system. At first the following localized ansatz was considered (see works \([2, 3, 4, 5, 6, 7, 8]\) and reviews \([9, 10, 11]\)):

\[
\Psi_0^c \approx e^{S_0} \prod_{\pi_c \ j=1}^{N} \varphi(r_j - R_j), \tag{2}
\]

where \( r_j \) and \( R_j \) are the coordinates of atoms and lattice sites, respectively, \( \pi_c \) means all possible permutations of coordinates \( r_j \). In all formulae for \( \Psi(r_1, \ldots, r_N) \) we omit the normalization constants. The function \( S_0 \) is usually written in the Bijl–Jastrow approximation \([12, 13, 14, 15]\):

\[
S_0 = \frac{1}{2} \sum_{j \neq j'} S_2(r_j - r_{j'}). \tag{3}
\]

The exact formula for \( S_0 \) is as follows \([16, 17]\):

\[
S_0(r_1, \ldots, r_N) = \frac{1}{2!} \sum_{j_1 \neq j_2} S_2(r_{j_1} - r_{j_2}) + \frac{1}{3!} \sum_{j_1 \neq j_2 \neq j_3} S_3(r_{j_1} - r_{j_2}, r_{j_2} - r_{j_3}) + \ldots
\]

\[
+ \frac{1}{N!} \sum_{j_1 \neq j_2 \ldots \neq j_N} S_N(r_{j_1} - r_{j_2}, r_{j_2} - r_{j_3}, \ldots, r_{j_{N-1}} - r_{j_N}). \tag{4}
\]

Here, the sum including \( S_j \) describes the \( j \)-particle correlations. In ansatz (2), the crystal lattice is postulated, and it is assumed that the atoms execute small oscillations near the sites. The function \( \varphi(r) \) from (2) in the approximation of small oscillations is \( \varphi(r) = e^{-\alpha r^2/2} \) \([2, 3, 4, 5, 6, 7, 8, 9]\). The simple analysis shows that, for such solution, no condensate of atoms is present \([10, 18, 19]\).

Later on, a wave ansatz was proposed \([20, 21, 22]\):

\[
\Psi_0^c \approx e^{S_0} e^{-\sum_{j=1}^{N} \theta(r_j)}, \tag{5}
\]

where function \( \theta(r) \) is periodic with periods of the crystal. This solution is of the wave type and is characterized by a condensate with WF \( \Psi_c(r) \approx e^{-\theta(r)} \). The crystal-like solutions with a condensate were considered in other approaches as well \([23, 24, 25, 26, 27, 28, 29, 30, 31, 32]\).
The third possible ansatz for GS of a crystal is as follows \[33, 34, 35, 36\]:

\[ \Psi_c^0 = e^{S_0}, \] (6)

\[ S_0(r_1, \ldots, r_N | k_r) = \frac{1}{2!} \sum_{j_1 \neq j_2} S_2(r_{j_1} - r_{j_2} | k_r) + \frac{1}{3!} \sum_{j_1 \neq j_2, j_2 \neq j_3} S_3(r_{j_1} - r_{j_2}, r_{j_2} - r_{j_3} | k_r) + \ldots \]

\[ + \frac{1}{N!} \sum_{j_1, j_2, \ldots, j_N} S_N(r_{j_1} - r_{j_2}, r_{j_2} - r_{j_3}, \ldots, r_{j_{N-1}} - r_{j_N} | k_r). \] (7)

It is a translationally invariant anisotropic solution. We denote the anisotropy of function (7) by a vector \( k_r \) (this is the reciprocal lattice vector with the nonzero smallest components). It is known that GS of a liquid or a gas is described by an isotropic WF (6), (4) \[15, 16, 17, 37, 38, 39\] (we consider the function (4) to be isotropic). It was assumed in a number of works that, at some critical density \( \rho = \rho_c \), the liquid solution (6), (4) spontaneously transforms into a crystalline solution (6), (7) \[33, 34, 35, 40\].

Let us clarify which of functions (2), (5) and (6), (7) can be the solution for a crystal. In order to verify the bulk structure of solutions, we can use any boundary conditions (BCs). Let us test the crystal solutions (2), (5), and (6), (7) for periodic BCs. The periodic system is translationally invariant, which yields two consequences. (i) The properties of a system on a ring must not change at a rotation of the ring. This holds provided that, at a displacement of the system as a whole by the radius-vector \( \delta r \to 0 \), WF of the system is multiplied by a constant:

\[ \Psi(r_1 + \delta r, \ldots, r_N + \delta r) = (1 + i\mathbf{p}\delta \mathbf{r})\Psi(r_1, \ldots, r_N) = e^{i\mathbf{p}\cdot\delta\mathbf{r}}\Psi(r_1, \ldots, r_N). \] (8)

(ii) Since

\[ \Psi(r_1 + \delta r, \ldots, r_N + \delta r) = \left( 1 + \delta r \sum_j \frac{\partial}{\partial r_j} \right) \Psi(r_1, \ldots, r_N), \] (9)

relation (8) yields

\[ \hat{P}\Psi \equiv -i\hbar \sum_j \frac{\partial}{\partial r_j} \Psi = \hbar\mathbf{p}\Psi. \] (10)

Therefore, the full collection of WFs \( \Psi_j(r_1, \ldots, r_N) \) of such a boundary-value problem can be constructed so that each WF is an eigenfunction of the momentum operator \( \hat{P} \), i.e., it satisfies conditions (8) and (10). This is well known from quantum mechanics.

The most widely used ansatz is WF (2), where the coordinates of sites \( \mathbf{R}_j \) are fixed and the same ones at any possible values of the atomic coordinates \( \{r_j\} \) (including the sets \( \{r_j\} \) and \( \{r_j + \mathbf{a}\} \) \[3, 5, 6, 9, 10, 11\]. Such ansatz does not satisfy conditions (8) and (10). Indeed, for \( \varphi(\mathbf{r}) = e^{-\alpha^2 r^2/2} \) we have

\[ \hat{P}\Psi_c^0 = i\hbar\alpha^2 \Psi_c^0 \sum_j (r_j - R_j) \neq \hbar\mathbf{p}\Psi_c^0. \] (11)
With regard for the anharmonic corrections to $\varphi(r)$, the formula for $\hat{P}\Psi_0^c$ is complicated, but the conclusion does not change. More complicated modification of WF (2) was proposed in [41]. For it, relation (10) does not hold as well.

Solution (2) is impossible for periodic BCs also because the concentration of a periodic Bose system is an exact constant: $n(r) = \text{const}$ [31 42 43 44]. This surprising property is related to the translation invariance and can be easily proved (for any pure state with a definite momentum, including the lowest state ($T = 0$), see the calculation of the density matrix in the coordinate representation in [44] and in the operator approach in [31]; for $T > 0$, this can be proved analogously to the analysis in [44], using the formula $n(r) = \text{const} \cdot \int dr_2 \ldots dr_N \sum_j e^{-E_j/k_BT}|\Psi_j(r, r_2, \ldots, r_N)|^2$ and property (8)). The constancy of the density means that, in a periodic system, the crystalline ordering is hidden. It must manifest itself in oscillations (with the period of a crystal) of the two-particle density matrix $g_2(r_1, r_2)$, rather than in the density. But solution (2) corresponds exactly to the oscillating particle density:

$$n(r + b) = n(r),$$

where $b_x, b_y, b_z$ are the sizes of crystal cell. [Let us show it. Since $S_0$ in (3) and (4) correspond to a constant density, we set $S_0 = 0$ in (2). Then we get $n(r) = C \cdot \sum_j e^{-\alpha^2(r-R_j)^2} \neq \text{const}$.

On the other hand, $n(r + b) = n(r)$, since the translation of the crystal by one step is equivalent to the renumbering of sites, which does not change the sum.]

For the wave ansatz (5), we obtain

$$\hat{P}\Psi_0^c = \Psi_0^c i\hbar \sum_j \frac{\partial \theta(r_j)}{\partial r_j}. \quad (12)$$

This equals $\hbar p\Psi_0^c$, if $\theta(r_j) = -ipr_j/N + \text{const}$. The ground state must correspond to $\hbar p = 0$ (see below). We get $p = 0$ at $\theta(r_j) = \text{const}$. Then ansatz (5) is reduced to the solution (6) with $S_0$ [41]. However, it is a solution for WF of the ground state of a uniform and isotropic system (liquid or gas) [15 16 17 37 38 39].

It is important that the WF of the ground state of a crystal (or liquid) with periodic BCs must correspond to zero momentum: $\hbar p = 0$. The case $\hbar p \neq 0$ is unphysical. Indeed, if the crystal would contain a quasiparticle, then the momentum $\hbar p \neq 0$ would be associated with this quasiparticle. But the ground state contains no quasiparticles, and the crystal as a whole does not move. Therefore, the separated direction that is set by nonzero momentum cannot be associated with a physical property. In view of this, we have $p = 0$.

This can be shown mathematically. Hamiltonian [11] commutes with the operator of inversion $\hat{I}$ and the operator of total momentum $\hat{P}$, but two last operators do not commute with each other. According to the well-known theorem of quantum mechanics [45 46], each energy level of such a system should be degenerate. The exception is the energy level corresponding to the zero momentum. Indeed, let the state $\Psi_1$ correspond to the momentum $\hbar p_1$ and the energy $E_1$: $\hat{P}\Psi_1 = \hbar p_1\Psi_1$ and $\hat{H}\Psi_1 = E_1\Psi_1$. Let us act by the inversion operator on the equation $\hat{H}\Psi_1 = E_1\Psi_1$. Since $\hat{I}\hat{H} = \hat{H}\hat{I} = 0$, we get $\hat{H}\hat{I}\Psi_1 = E_1\hat{I}\Psi_1$.
That is, the state \( \hat{I} \Psi_1(r_1, \ldots, r_N) \equiv \Psi_1(-r_1, \ldots, -r_N) = \Psi_2(r_1, \ldots, r_N) \) corresponds to the same energy as that of the state \( \Psi_1(r_1, \ldots, r_N) \). If \( \Psi_1 \) satisfies periodic BCs, then \( \Psi_2 \) satisfies the same ones. On the other hand, if \( \hat{P} \Psi_2(r_1, \ldots, r_N) = \hbar p_1 \Psi_1(r_1, \ldots, r_N) \), then \( \hat{P} \Psi_2(r_1, \ldots, r_N) \equiv \hat{P} \Psi_1(-r_1, \ldots, -r_N) = -\hbar p_1 \Psi_2(r_1, \ldots, r_N) \). In other words, the state \( \Psi_2 \) is characterized by the momentum \( -\hbar p_1 \). Since the states \( \Psi_1 \) and \( \Psi_2 \) correspond to different momenta, they are physically different states. Hence, the level \( E_1 \) is degenerate. Only at \( p_1 = 0 \) the states \( \Psi_1 \) and \( \Psi_2 \) are characterized by the identical energies and momenta. Such states are equivalent. In this case, the level \( E_1 \) is non-degenerate. If WF \( \Psi_1 \) corresponds to the energy \( E_1 \) and does not correspond to a definite momentum, it can be expanded in WFs of states with a definite momentum and the energy \( E_1 \). Such expansion must contain at least one WF with \( \hbar p \neq 0 \), i.e., the state \( \Psi_1 \) is degenerate. However, GS must be non-degenerate [47]. Thus, the genuine GS can correspond only to zero momentum.

The structure of WF of the ground state, \( \Psi_0 \), of a Bose system with periodic BCs can be easily determined. The condition \( p = 0 \) and formulae (8) and (10) imply that \( \Psi_0 \) should not vary at a translation. Therefore, it can depend only on the difference of coordinates. The general form of such nodeless function is given by formulae (6), (1) or (6), (7). This can be proved strictly (see [39] and Appendix 1 below).

It is interesting to note that the structure of \( \Psi_0 \) (6), (1) of a quantum liquid is usually obtained from the requirement that \( \Psi_0 \) should be invariable at a translation [\( \hat{p} = 0 \) in (8)] [16, 39]. However, the translation invariance of a system admits \( p \neq 0 \) in (8). Apparently, it was not shown previously in the literature that the Bose system with \( p \neq 0 \) does not correspond to GS. This was proved above. Therefore, the condition \( p = 0 \) is primary, and the translation invariance of \( \Psi_0 \) is a consequence of this requirement.

Note also that, in a series of articles [35, 40, 48, 49, 50], Bose liquid and Bose crystal were described by a “shadow” WF (SWF)

\[
\Psi(R) = \int e^{-\Xi(R, S)} dS, \quad R \equiv r_1, \ldots, r_N, \quad (13)
\]

\[
\Xi(R, S) = \sum_{j_1 < j_2} u_r(|r_{j_1} - r_{j_2}|) + \sum u_{sr}(|r_k - s_k|) + \sum_{j_3 < j_4} u_s(|s_{j_3} - s_{j_4}|), \quad (14)
\]

where \( S \equiv s_1, \ldots, s_N \) are “shadow” variables. If \( u_r, u_{sr}, u_s \) are represented in the form of Fourier series, then SWF (13), (14) becomes translationally invariant. Since any nodeless translationally invariant WF can be written in the form of (6), (1) or (6), (7), function (13), (14) is a partial case of the general solution (6), (1) [or (6), (7)] written in a different form. This was noted in reviews [35, 36]. In this case, SWF has a relatively simple structure and, apparently, enables one to indirectly involve, at least partially, all higher correlation corrections [35]. The authors of works [35, 40, 48, 49, 50] assert that SWF (13), (14) describes a Bose liquid at some densities and a Bose crystal at other ones. This is equivalent to the assumption that, at some \( \rho = \rho_c \), the liquid solution (6), (1) spontaneously transforms into a crystalline solution (6), (7).

\( \hat{I} \) and \( \hat{P} \)
We have shown above that the ground state of a periodic system of interacting spinless bosons corresponds to zero momentum. Among four above-considered solutions (liquid solution and three crystalline ones), this requirement is satisfied by the liquid solution (6), (4) and the crystalline one (6), (7). The other two crystalline solutions, (2) and (5), describe the states without a definite momentum. Hence, only WF (6), (7) can be an exact solution for GS of a crystal with periodic BCs. The key question is as follows: Can such crystalline solution exist?

2.2 Degeneracy of an anisotropic state

The available literature gives no answer to the above question, to our knowledge. Apparently, it is impossible to find it analytically. The numerical methods also do not give an exact answer because they give incomplete information. However, the answer can be found by means of the symmetry analysis considered in what follows. Two other methods are proposed in [51, 52].

Hamiltonian (1) of the 3D system is invariant under the group of orthogonal transformations $O(3) = SO(3) \times C$, consisting of the group of rotations $SO(3)$ and the group of inversions $C$ (it contains two elements: inversion $I$ and $I^2 = 1$; here and below, we consider that any symmetry transformation is applied to all coordinates $r_1, \ldots, r_N$). This invariance is preserved if $\hat{H}$ also includes a three-particle interaction $[53, 54, 55, 56]$. Therefore, $\hat{H}$ commutes with the operator of rotation $\hat{R} = e^{i \varphi \hat{L}/\hbar}$ [45, 46, 57], where $\hat{L}$ is the operator of total angular momentum of the system, $\varphi$ is a rotation angle, and the unit vector $\hat{i}_\varphi$ sets the rotation axis. Hence, $[\hat{H}, \hat{L}] = 0$, and $[\hat{H}, \hat{L}^2] = 0$. Since the operators $\hat{H}, \hat{L}^2$ and $\hat{L}_z$ commute with each other, the complete set of eigenfunctions can be constructed so that those functions be the eigenfunctions of these three operators [45, 46]. It is important that BCs must admit this (as a rule, this point is not mentioned in textbooks). Therefore, we consider the system to be infinite (closed or not) or finite ball-shaped. In the first case, BCs are invariant under the translations and rotations, which corresponds to the uniformity and isotropy of the space. This gives the laws of conservation of the momentum and angular momentum [45, 46]. If BCs would not be uniform and isotropic at infinity, then the laws of conservation of the momentum and angular momentum would not hold in our world. For a finite ball, BCs are invariant only under the rotations. In both cases, since the Hamiltonian and BCs are invariant with respect to the rotations, WFs can be set so that they are transformed by the irreducible representations of the rotation group $SO(3)$ [57, 58]. This group is characterized by the complete collection of irreducible representations $g \rightarrow \hat{T}_l(g)$ with $l = 0, 1/2, 1, 3/2, 2, \ldots, \infty$ and the dimension $2l + 1$ (here, $g$ is an element of the group). The representations with integer and half-integer $l$ are, respectively, one- and two-valued [57, 59, 60]. The scalar WFs can be transformed only by the representations with integer $l$. In this case, $\hat{L}^2 \Psi^{(l)}(\hat{r}) = \hbar^2 l(l + 1) \Psi^{(l)}$ [57, 58]. The operator of rotation is defined by the formula [45, 46]

$$\hat{R} \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N | \mathbf{k}) = \Psi(\hat{r}_1, \ldots, \hat{r}_N | \mathbf{k}),$$ (15)
where \( \mathbf{r}_j \) and \( \mathbf{r}'_j = A \mathbf{r}_j \) are the coordinates of a vector before and after a rotation, \( A \) is the rotation matrix (the vectors \( \mathbf{r}_j \) and \( \mathbf{r}'_j \) are set in the same basis). The operator \( \hat{R} \) transforms the coordinates and does not affect constants like \( \mathbf{k} \) that characterize a possible anisotropy of the system. Eq. (15) leads to the formula \( \hat{R} = e^{iA} \mathbf{L}/\hbar \). The wave functions invariable relative to any rotation \( (\hat{R}\Psi \equiv e^{iA} \mathbf{L}/\hbar \Psi = \Psi, \text{i.e., } \hat{L}\Psi = 0) \) are transformed by the identical (unit) representation \( g \rightarrow T_0(g) \): \( T_0(g)\Psi = \Psi \) for any element \( g \) of the group \( SO(3) \). The crystalline GS is anisotropic. Therefore, \( \hat{R}\Psi \neq \Psi, \hat{L}\Psi \neq 0 \). Such state is transformed by one or several representations \( g \rightarrow T_l(g) \) with \( l \neq 0 \). The irreducible representation \( g \rightarrow T_l(g) \) is characterized by the orthonormalized basis \( \Psi^{(l)}_1, \Psi^{(l)}_2, \ldots, \Psi^{(l)}_{2l+1} \).

In this case, \( T_l(g)\Psi^{(l)}_j = \sum_{p=1}^{2l+1} T_{pj}^{(l)}(g)\Psi^{(l)}_j \) for any element \( g \) of the group \( SO(3) \), where \( T^{(l)}_j(g) \) are the matrices of constants and realize the representation \( g \rightarrow T_l(g) \). For each representation \( g \rightarrow T_l(g) \), all functions correspond to the same energy. Indeed, let WF \( \Psi^{(l)}_j \) be an eigenfunction of the Schrödinger equation with energy \( E \):

\[
\hat{H}\Psi^{(l)}_j = E\Psi^{(l)}_j.
\]

Let us act by the operator \( \hat{T}(g) = \hat{R}^{-1}(g) = \hat{R}(g^{-1}) \) on this equation. Since \( \hat{R}(g)\hat{H} - \hat{H}\hat{R}(g) = 0 \) for any rotation \( g \), the last equality holds also for the rotation \( g^{-1} \). From whence, we get \( \hat{T}(g)\hat{H} - \hat{H}\hat{T}(g) = 0 \). Therefore,

\[
E\hat{T}(g)\Psi^{(l)}_j = \hat{T}(g)E\Psi^{(l)}_j = \hat{T}(g)\hat{H}\Psi^{(l)}_j = \hat{H}\hat{T}(g)\Psi^{(l)}_j.
\]

That is, the function \( \hat{T}(g)\Psi^{(l)}_j \) is also an eigenfunction of the Schrödinger equation with energy \( E \). We now substitute the expansion \( \hat{T}(g)\Psi^{(l)}_j = \sum_p \hat{T}_p(g)\Psi^{(l)}_j = \hat{T}_l(g)\Psi^{(l)}_j = \sum_{p=1}^{2l+1} T^{(l)}_p(g)\Psi^{(l)}_j \) in formula (17). Since the basis functions \( \Psi^{(l)}_p \) are independent of one another, we get that all functions \( \Psi^{(l)}_p \) are eigenfunctions of the Schrödinger equation with energy \( E \). Therefore, such state is \((2l+1)\)-fold degenerate. WF of a crystal \( \Psi(r_1, \ldots, r_N|k_r) \) may not coincide with the function \( \Psi^{(l)}_p \). Then it is necessary to expand \( \Psi(r_1, \ldots, r_N|k_r) \) in the basis functions \( \Psi^{(l)}_p \) of all irreducible representations corresponding to the energy of the crystal. In this case, the degeneracy multiplicity is equal to the sum of the dimensions \( 2l+1 \) of all these representations. Thus, only the isotropic state is not degenerate. It is the state that transits into itself at any rotation and is transformed by the unit representation of the group \( SO(3) \). Since the genuine GS of a Bose system is non-degenerate (see also Appendix 2 below), it should correspond to an isotropic state. In Appendix 1 it is shown that \( \Psi_0 \) corresponds to \( \hat{L}\Psi_0 = 0 \) and, therefore, is isotropic. Thus, we have proved that any anisotropic state of an infinite (or finite ball-shaped) 3D system of spinless bosons is degenerate and, therefore, does not correspond to the genuine GS of the system.

WFs of a many-boson system are usually constructed as eigenfunctions of the momentum operator \( [38, 39, 61, 62, 63, 64] \). In this case, WF of any excited state of a periodic system of \( N \) bosons can be written in the form \( [61, 65] \) (see also Appendix 1)

\[
\Psi_p(r_1, \ldots, r_N) = \psi_p\Psi_0,
\]
\[ \psi_p = b_1(p)\rho_{-p} + \sum_{q_1 \neq 0} \frac{b_2(q_1; p)}{2!N^{1/2}} \rho_{q_1}\rho_{-q_1-p} + \ldots + \]

\[ + \sum_{q_1, \ldots, q_{N-1} \neq 0} \frac{b_N(q_1, \ldots, q_{N-1}; p)}{N!N^{(N-1)/2}} \rho_{q_1} \cdots \rho_{q_{N-1}} \rho_{-q_1-\cdots-q_{N-1}-p} \]  

(19)

with \( \Psi_0 \) (6), (4). Formulae (18) and (19) are exact. Solution (18), (19) describes states with one, two, or many interacting phonons (or rotons), depending on the coefficients \( b_j \) (65). WF (18), (19) corresponds to the momentum \( \hbar p \). The translation \( \{r_j\} \rightarrow \{r_j + a\} \) transfers solution (18) into the equivalent solution: \( \Psi_p(r_1, \ldots, r_N) \rightarrow e^{i\hbar a P/\hbar} \Psi_p(r_1, \ldots, r_N) \). Such approach assumes that \( \hat{H} \) is invariant under translations and, therefore, commutes with the operator of translations \( \hat{T} = e^{i\hbar a P/\hbar} \) and the operator of total momentum \( \hat{P} \). In view of this, one can find the complete set of orthogonal functions, being the eigenfunctions of the operators \( \hat{H} \) and \( \hat{P} \) (it differs from the complete set for the operators \( \hat{H}, \hat{L}_2 \), and \( \hat{L}_z \), since \( \hat{P} \) and \( \hat{L}_z \) do not commute with each other). Functions (18) with all possible \( p \) and the function \( \Psi_0 \) (6), (4) realize such a set (39, 61, 65). It can be called a P-set. Earlier, the analysis of crystalline solutions was performed only within the P-approach. Apparently, this is why the degeneracy of the anisotropic state was not noticed.

The many-boson systems are usually described in the P-approach, since it is simpler and more physical (as a rule, a quasiparticle is characterized by a definite momentum, rather than an angular momentum). The L-set of eigenfunctions is used for the description of the electron shell of an atom. For many-boson systems, the L-approach was used rarely and only for the corresponding BCs (66, 67). If BCs admit both approaches, then any WF from the P-set can be expanded in the complete set of WFs from the L-set, and vice versa. Interestingly, \( \Psi_0 \) (6), (4) belongs simultaneously to the P- and L-set of WFs. This function is transformed by the unit representations of the \( SO(3) \) group and the group of translations \( T(3) \).

Thus, for two types of systems (finite ball-like and infinite ones), we have shown that the crystal solutions do not contain the genuine (nodeless) GS and, therefore, do not form the complete set of eigenfunctions of the Schrödinger boundary-value problem. The genuine GS correspond always to the liquid solution. Based on the liquid GS, one can construct a set of excited liquid states. The group \( SO(3) \) contains, as subgroups, point groups corresponding to seven types (syngonies) of crystal lattices. Therefore, it is obvious that, for two indicated types of systems, the complete set of WFs of the Schrödinger boundary-value problem contains all solutions for each syngony and all solutions for a liquid. The lowest state of a crystal of each type must correspond to WF with a large number of nodes. For the infinite system such a solution can be rotated by any angle, then we will apparently obtain another solution of the same boundary-value problem (51). That is, the complete set of WFs of a Bose system should contain solutions for crystals of all possible types, including the infinite number (for the infinite system) of all admissible rotated solutions of each type. In this case, the collection
of solutions for a crystal with fixed lattice and orientation contains the infinite number of WFs, but is an infinitely small part of the complete collection of WFs of the boundary-value problem. The latter can be found by means of the construction of the general system of eigenfunctions of the operators $\hat{H}$, $\hat{L}^2$, and $\hat{L}_z$ or (for the infinite system) the operators $\hat{H}$ and $\hat{P}$. It is known that each type of crystals is stable at definite densities. In such interval of densities, the lowest state of a crystal must correspond to a local statistical-thermodynamic minimum of the energy in the space of states (this is the minimum in the sense that small perturbations of a crystal increase its energy). Otherwise, the crystal would be unstable. In this case, the absolute minimum corresponds to a liquid (see Fig. 1).

Fig. 1: [Color online] The lower and upper minima correspond to a liquid and a crystal, respectively. $E$ is the internal energy of a Bose system, $s$ marks quantum states $\Psi_j(r_1,\ldots,r_N)$ of the system corresponding to the same concentration $n = N/V$. $E$ and $s$ are given in arbitrary units.

For clarity, consider the following example. Assume that the Hamiltonian $\hat{H}_c$ of a Bose system contains an external potential $U_c$ corresponding to a point symmetry group of a crystal of some type:

$$\hat{H}_c = -\frac{\hbar^2}{2m} \sum_{j=1}^N \Delta r_j + \frac{1}{2} \sum_{l\neq j} U(|r_l - r_j|) + U_c(r_1,\ldots,r_N).$$

In this case, the Hamiltonian is characterized by two symmetries: the continuous group $O(3)$ and a discrete group that is a subgroup of the group $O(3)$ and corresponds to the potential $U_c$. It is clear that if $U_c$ sets a very deep well on the place of each lattice site, then the structure of low-lying states must be defined by the potential $U_c$. That is, all WFs of low-lying states must be transformed by irreducible representations of the discrete group of the crystal. In this case, the crystalline solutions apparently form the complete set of eigenfunctions of the given boundary-value problem, and GS of the crystal should correspond to the nodeless non-degenerate GS of the system. As the potential $|U_c|$ decreases, the solutions for WFs should approach those for the unperturbed Hamiltonian (1). If the potential $U_c$ is weak relative to the interatomic one, then the structure of all WFs has to be determined by the group $O(3)$.
Therefore, we may expect that, at some small finite $U_c$, WFs acquire the structure of WFs of the unperturbed Hamiltonian (11). We may expect that, in this case, the nodeless GS corresponds to a liquid at any density, and the weak potential $U_c$ changes insignificantly the solutions corresponding to Hamiltonian (11). As $U_c$ decreases to an infinitely small value, the solutions should coincide with those for Hamiltonian (11).

We mention the idea to obtain the crystal nodeless GS from a liquid GS as a result of the spontaneous breaking of the translational and rotational invariances of the Hamiltonian (11) due to the introduction of an infinitely small crystal potential $U_c$ in (11) [9, 68]. In our opinion, such mechanism does not work. Indeed, it was supposed in [9, 68] that the constant density (liquid GS) arises due to the averaging over many configurations that differ from one another only by translations. Therefore, the removal of the translational invariance could lead to the crystal nodeless GS with oscillating density. We think that this reasoning is not quite correct. We note that, under a translation WF (18), (19) is only multiplied by a unit modulus constant. Therefore, all states differing from one another only by translations enter the statistical sum as one state. In other words, there is no averaging over such states. Moreover, the constant density is characteristic of any WF (18), (19). The crystalline nodeless GS cannot be obtained as a result of the spontaneous choice of one of solutions (18), (19), or (6), (4), since the crystalline nodeless WF is simply absent among those WFs: At any density, the nodeless WF corresponds to a liquid, as is shown above.

Note that Hamiltonian (11) is also invariant under the group of permutations $S_N$. It is of interest that any symmetric Bose solution is transformed by the identical (unit) representation of the group $S_N$. Thus, the isotropic solution (6), (4) realizes the most symmetric state of an infinite periodic system. This state is invariant with respect to all groups of symmetries of the Hamiltonian: $O(3)$, $T(3)$, and $S_N$. Apparently, for any BCs the ground state corresponds to the most symmetric solution that is transformed by the unit representations of all groups of symmetries of the boundary-value problem [58]. Indeed, such a solution is non-degenerate and changes most smoothly in space. Therefore, it should correspond to the lowest energy.

We note also that for a finite ball the Hamiltonian and BCs are characterized by the symmetry group $O(3) \times S_N$. Therefore, GS should be invariant with respect to these groups, which corresponds to a liquid state. Thus, the lowest state of a finite crystal ball corresponds to WF with nodes for any parameters of the system.

In the above reasoning, the degeneracy is related to the noncommutativity of the operators $\hat{L}_x, \hat{L}_y, \hat{L}_z$. In work [51], the degeneracy of an anisotropic state was proved for an infinite Bose system with the help of a general quantum-mechanical analysis. In this case, the degeneracy is related to the noncommutativity of the operators $\hat{L}$ and $\hat{P}$. In the two-dimensional (2D) case, $\hat{L}$ has only the component $\hat{L}_z$. In this case, only the proof from work [51] is valid.

We now make some remarks about the method in use. It is impossible to find the wave functions for a many-particle system of complicated shape. Therefore, it is reasonable to take
such BCs and such size of the system for which the solution can be most easily found. The
properties of a macroscopic system should not depend on the shape of boundaries and should
not vary at an increase of the system sizes to infinity (at a constant density). Therefore, we
considered the systems that are the simplest for the symmetry analysis: the infinite system
under periodic BCs and a finite ball-shaped one under zero BCs. For clarity, it would be
useful to give the general solution in the $L$-approach (besides the solutions (18), (19) in the
$P$-approach). However, such solutions have not been found in the available literature. The
degeneracy of an anisotropic state of the infinite system can be seen without calculations: if
the isotropic WF $\Psi_0$ at some density transits spontaneously to an anisotropic WF $\Psi'_0$
with a separated vector $k$, then exactly the same solutions $\Psi'_0$ with a vector $k'$ ($|k'| = |k|$)
of all possible directions must exist due to the isotropy of space. We obtain the infinite-fold
degeneracy. For a finite system, the degeneracy is always finite [47]. This is due to BCs. For
example, for the periodic BCs, the momentum of the system of quasiparticles can have only
discrete values. Therefore, it can be “turned” only by certain discrete angles.

For a visual image we give several known anisotropic solutions for an infinite periodic Bose
system. The solutions for a liquid with one and two phonons in the zero approximation reads
$\Psi_k(r_1, \ldots, r_N) = \rho_{-k} \Psi_0$ [12, 37, 38, 61] and $\Psi_{k_1,k_2}(r_1, \ldots, r_N) = \rho_{-k_1,} \rho_{-k_2} \Psi_0$ [65, 69, 70],
respectively. These solutions are infinite-fold degenerate with respect to rotations. The
crystal solution for such a system was proposed in [51]. It is also infinite-fold degenerate.
In all these cases the degeneracy is caused by that the Hamiltonian $\hat{H}$ (1) commutes with
the operators $\hat{L}$ and $\hat{P}$, which do not commute with each other. Visually, the degeneracy is
related to the equivalence of all directions in space.

### 2.3 Possible exact ansatz for the ground state of a Bose crystal

Let us try to find WF of a zero-temperature crystal. We will call a zero-temperature state
of a crystal the ground state of a crystal. It is obvious that the weakly excited states of the
Bose system cannot correspond to a crystal. In particular, the solution for the liquid state
with one phonon in the zero approximation reads [12, 37, 38, 61, 71]

$$\Psi_k(r_1, \ldots, r_N) = \rho_{-k} \Psi_0, \quad \Psi_0 = e^{S_0}$$

(for periodic BCs). The solution for a two-phonon liquid state under the same BCs in the
zero approximation is [65, 69, 70]

$$\Psi_{k_1,k_2}(r_1, \ldots, r_N) = \rho_{-k_1} \rho_{-k_2} \Psi_0.$$  \hspace{1cm} (22)

Therefore, it is clear that GS of a crystal should correspond to a highly excited state of the
Bose system. In addition, it is natural to expect that the network of nodes of WF does not
change at the displacement of the crystal by the lattice period. The solution for GS of a
crystal can be easily guessed for a simple rectangular lattice with $N \to \infty$ and the zero BCs
(Ψ = 0 at x = 0; L_x, y = 0; L_y, z = 0; L_z) [72]:

\[ \Psi_0^c = e^{S_0 + S_c} \prod_{j=1}^N \{ \sin (k_{l_x} x_j) \sin (k_{l_y} y_j) \sin (k_{l_z} z_j) \}. \]  

(23)

Here, the product of sines directly sets the crystal lattice (we suppose that faces coincide with lattice planes), \((k_{l_x}, k_{l_y}, k_{l_z}) = (l_x \pi / L_x, l_y \pi / L_y, l_z \pi / L_z) = (\pi / a_x, \pi / a_y, \pi / a_z)\), \(a_x, a_y, a_z\) are the periods of the lattice, \(l_x, l_y, l_z\) are integers, \(L_x, L_y, L_z\) are sizes of the crystal; and \(S_c(r_1, \ldots, r_N)\) is a correction function. Function (23) has a wave structure, but possesses a lot of nodes, in contrast to (5). Near any maximum \(x_0\), the function \(\sin(kx)\) can be represented as \(e^{-\alpha x^2 / 2}\). This allows us to theoretically get the fitting constant \(\alpha\) with reasonable accuracy [72]. Furthermore, if we use \(\varphi(r) = -\alpha^2 x^2 / 2 - \alpha^2 y^2 / 2 - \alpha^2 z^2 / 2\) in (2) instead of \(\varphi(r) = -\alpha^2 r^2 / 2\), then those configurations, for which the atoms are located near the lattice sites, are described by functions (23) and (2) equally (a more complicated “nondiagonal” function \(\varphi(r)\) was considered in [11, 73]). On the whole, WF (2) can be considered as a fairly good zero approximation. This property, jointly with fitting parameters, enables one to explain with the help of WF (2) some experimental properties of crystals [6, 74]. However, the general structure of the wave function is represented by ansatz (2) incorrectly. In particular, ansatz (2) loses the condensate of atoms \(\Psi_c(r) \simeq \sin (k_{l_x} x) \sin (k_{l_y} y) \sin (k_{l_z} z)\) which follows from WF (23). Moreover, ansatz (2) does not catch that GS of a crystal has to be higher by energy than GS of a liquid (see Fig. 1).

Note that a possible ansatz for GS of a crystal with periodic BCs was proposed in [51].

Comparing WF (23) with the one-phonon (21) and two-phonon (22) solutions for a liquid, we see that GS of a crystal with the zero BCs corresponds to a liquid with \(N\) identical quasiparticles with quasimomentum \(k_1\). That is, GS of a crystal can be considered as a liquid with a condensate of quasiparticles. In this case, namely the condensate of quasiparticles creates a crystal lattice in the medium. As was mentioned above, GS (23) contains also a condensate of atoms with quasimomentum \(k_1\). Small deviations from GS of a crystal correspond to a crystal with several quasiparticles or defects. The temperature \(T\) of a crystal can be introduced in the ordinary way with the help of the partition function, by connecting \(T\) with quasiparticles.

We note that the solutions for a crystal that are characterized by a condensate of atoms with quasimomentum \(k \neq 0\) were considered previously [23, 24, 26, 27, 28, 31]. However, it was assumed in those works that, in addition to such “coherent crystal” [27, 28], there exists the “ordinary crystal” with nodeless ground-state WF and without a condensate. But the above analysis shows that such “ordinary crystal” is impossible, at least for an infinite system. Moreover, the idea of that a crystal is formed by a condensate of quasiparticles with quasimomentum \(2\pi / a_x\) [in one dimension (1D)] was advanced in [25]. It is similar to the above conclusion, but the quasiparticles here and in [25] are different. In function (23), the quasiparticles are introduced relative to the genuine liquid GS of the system, whereas the
quasiparticles in [25] are considered relative to GS of a crystal.

The above analysis uses an anisotropy and is not suitable for a 1D space. In the recent work [52], the exact solutions were found for a 1D system of point bosons with a small value of $N$. In this case, the crystalline solution agrees with formula (23). We are not aware of other exact solutions for a 1D crystal which is not placed in a trap field. On the other hand, for the 1D system of dipolar bosons, the crystal regime was numerically found for the genuine nodeless GS (see the recent work [75] and references therein). Thus, in one dimension, the genuine GS can be either a liquid or a crystal, depending on the nature of the interatomic interaction and on parameters of the system.

We have noted above that the properties of a macroscopic system should not depend on the shape of boundaries. It is a commonly accepted assumption. However, it is not proved in the general case. In our opinion, we cannot omit, in principle, the possibility of a strong influence of boundaries as a topological effect. But we do not know works, where a similar effect is accurately found. The available solutions show that the boundaries exert a negligible influence on the bulk properties of a Bose liquid such as the energy of GS (see the solutions for the periodic [37, 39, 76, 77], zero [78, 79, 80], and mixed [81] BCs) and the dispersion law of quasiparticles [80, 82, 83]. In this case, the solutions [76, 77, 78, 79, 81, 82] are exact. Based on the above-executed analysis and those solutions, we assume that the genuine GS of a Bose system corresponds to a liquid at any shape of boundaries, any density, and any dimensionality of a system.

Monte Carlo solutions for Bose crystals are discussed in Appendix 3. The nature of GS of a Bose system can be clarified by the multiconfiguration time-dependent Hartree method [84] that allows one to find a solution with good accuracy for a 1D system of $N \lesssim 10$ bosons. Apparently, the last modifications of this method [85] enable one to study even 2D systems of $N \lesssim 10$ bosons. This method is also suitable for the study of the transition from the crystalline genuine GS to the liquid one, as the bare crystal potential $U_c$ decreases, for 1D and 2D systems of $N \lesssim 10$ particles. Such results would be valuable.

As is seen, the properties of Bose crystals are, apparently, much more complex and interesting, than it follows from the “naive” WF [2].

### 3 Physical consequences

On the basis of the above analysis, we assume that, for any BCs, the inequality

$$E^c_0(\rho, N) > E^l_0(\rho, N)$$

holds. Here, $E^c_0$ and $E^l_0$ are the energies of GS of a Bose crystal and a Bose liquid, respectively, $N$ is the number of atoms, and $\rho = mn$ is the density. In [23], $E^c_0$ and $E^l_0$ are compared at the same $\rho$. However, the phase transitions occur in experiments at the same pressure $P$. 
Here, two cases are possible:

\[ E_0^c(P, N) > E_0^l(P, N) \]  \hspace{1cm} (25)

or

\[ E_0^c(P, N) < E_0^l(P, N). \]  \hspace{1cm} (26)

For \(^4\text{He},\) inequality (25) is satisfied (at the pressure of crystallization \(P \approx 25 \text{ atm},\) see Appendix 3). The liquid satisfying condition (25) must be stable against crystallization, at low \(P\) and \(T.\) If (26) is satisfied, the liquid corresponds to a metastable state, but the duration of the transition into the stable crystalline state may be long.

Inequality (24) testifies to the existence of a large number of quantum states corresponding to a liquid and possessing the energies less than the GS energy of a crystal. We will call such states “under-crystal liquid” (“underliquid” for short). Since this region of states is large, one can expect that at least part of it is observable. It is also clear that, at sufficiently low temperatures, the underliquid has to be superfluid. The creation of such superfluids will mean that, in addition to the vessels with He II, physical laboratories will possess the vessels with other superfluids. Let us try to ascertain how the underliquid can be produced.

For all known liquids, except for \(^4\text{He},\) the \((P,T)\) phase diagram is separated into the regions corresponding to a gas, a liquid, and a crystal and has the triple point (see Fig. 2). The \((P,T)\) diagram of \(^4\text{He}\) has no triple point: the gas contacts only with the liquid. Each of the transitions (gas–liquid, liquid–crystal, and gas–crystal) is operated by three equations describing the equilibrium between phase 1 and phase 2 [86]:

\[ P_1 = P_2 \equiv P, \quad T_1 = T_2 \equiv T, \]

and

\[ P(v_1 - v_2) + T[s_2(P, T) - s_1(P, T)] = E_2(P, T) - E_1(P, T), \]  \hspace{1cm} (27)

where \(E_j\) is the internal energy per atom for the system staying in the \(j\)-th phase, \(v_j\) and \(s_j\) are the volume and entropy (per atom) of the \(j\)-th phase. Equation (27) is equivalent to the equality of the chemical potentials of phases 1 and 2: \(\mu_1(P, T) = \mu_2(P, T).\)

The possible position of the underliquid region on the \((P,T)\) diagram is shown by stars in Fig. 2. The upper and lower boundaries of the underliquid region are set by condition (27). The lower boundary corresponds to the transition underliquid–gas. The possible upper boundary corresponds to the transition underliquid–crystal. In the limits of these boundaries, the liquid can be stable or metastable, as was noted above. The right boundary \(P_{ul-c}(T)\) is shown in Fig. 2 approximately. It corresponds not to a phase transition, but to the condition \(E^l(P, T) = E_0^c(P)\) (that is possible, if (25) is satisfied). The equation for the lower boundary will be obtained in what follows. It is easy to estimate the location of the upper boundary \(P_{ul-c}(T).\) At \(T = 0,\) relation (27) yields

\[ P_{ul-c}(T = 0) = \frac{E_0^c(P) - E_0^l(P)}{v_l - v_c}. \]  \hspace{1cm} (28)
According to \[9\], the relation $k^2\xi^2 = 15\frac{k_B T}{\varepsilon}$ holds for the inert elements (here, $\varepsilon$ is the energy from the Lennard-Jones potential). Assume that $E_0^l(P = 0) = 0$ if $P, T \approx 0$. At low $T$, we may consider only the phonon contribution to the energy. Then $E^l(T) = E_0^l + \frac{\pi^2}{36} \left( \frac{k_B T}{\varepsilon} \right)^3 k_B T s$, where $c_s$ is the first sound velocity. The relations $E^l(P = 0, T) = E_0^l(P = 0)$ and $E_0^c(P = 0) - E_0^l(P = 0) \approx 0.15 k_B T_3$ yield

$$\frac{T^4}{T_3^4} \simeq \frac{30 \cdot 0.15 n \left( \frac{\hbar c_s}{k_B T_3} \right)^3}{\pi^2}.$$ \hspace{1cm} (29)

Using the parameters of the triple point for neon ($T_3 = 24.55 K$ \[88\], \[89\], \[90\]), $c_s = 628 m/s$, $\rho = 1.24 g/cm^3$ \[88\], \[91\]), we get $T \approx 0.6 T_3$. For liquid argon at the triple point, we have $T_3 = 83.81 K$ \[88\], \[89\], \[90\], $c_s = 870 m/s$, $\rho = 1.38 g/cm^3$ \[92\]. In this case, we obtain from (29) $T \approx 0.26 T_3$. We expect that these estimates of $T$ are valid by the order of magnitude.

The basic question is: How can we “get to” the region of underliquid in experiments? (The underliquid state of $^4$He has already been obtained: as it is easy to guess, this is He II.) On top and to the right from the region of underliquid, the crystalline states are placed. The region of underliquid corresponds to very low temperatures: $T \lesssim 0.5 T_3$. The crystalline

Fig. 2: [Color online] $(P, T)$ phase diagram for inert elements (H$_2$, Ne, Ar, etc., except for $^4$He) with the assumed region of the under-crystal liquid (bounded by stars ***): $lg \equiv \log_{10}$. Lines of the transitions gas–crystal (○ ○ ○, Eq. \[88\] with $\xi = 9.69$), gas–liquid (▲▲▲), and liquid–crystal (■■■) are shown. $P_3$ and $T_3$ are the pressure and temperature at the triple point. Dotted line (Eq. (40) with $\xi = 9.69, f = 7$) marks the continuation of the line gas–liquid to the region of low $T$. This curve lies somewhat higher than the curve ○ ○ ○, but the difference is visually indistinguishable (maximum distance between the curves along the vertical is equal to 0.13 and corresponds to $T/T_3 \approx 0.8$). The curves ▲▲▲, ■■■, and the right vertical boundary of the region of the under-crystal liquid are drawn by eye.

For the realistic values $v_l - v_c = 0.1 v_l = 0.1(3.6\text{Å})^3$ and $E_0^c(P) - E_0^l(P) = 10 K k_B$, we find $P_{ul-c}(T = 0) \approx 300 atm$ (here, $k_B$ is the Boltzmann constant). The upper boundary exists, if $P_{ul-c}(T = 0) > 0$. At $P_{ul-c}(T = 0) < 0$ the upper boundary is absent, which corresponds to Fig. 2. This case is considered below in more details.

We now estimate the temperature for the right boundary $(E^l(P, T) = E_0^c(P))$ at $P \approx 0$. We expect that these estimates of $T$ are valid by the order of magnitude.
states at such $T$ were experimentally studied for many substances, but the underliquid states were not found. According to (25) and (26), the crystal with $T$ and $P$ from the region of underliquid should be metastable or stable, respectively. In the metastable state, such crystals live, apparently, very long (otherwise, the underliquid would be found experimentally long ago). Therefore, we believe that it is impossible to produce an underliquid from a crystal (by decreasing $T$ or $P$).

The underliquid can be, apparently, obtained by strong supercooling of a liquid whose initial temperature is higher than the melting one. To avoid the crystallization, it is necessary to purify a liquid from impurities and to use a vessel with smooth walls (or to cover the walls with a special coating, see below). A shortcoming of the method consists in the necessity of a strong supercooling, which requires the high degree of smoothness of walls and of purity of a liquid.

It may be easier to get in the underliquid region by isothermal compression of a gas at $T \ll T_3$. According to Fig. 2, at the isothermal increase in the pressure of a gas with $T \ll T_3$, we cross firstly the curve gas–crystal and then the curve gas–liquid. Therefore, the gas must turn into a crystal (not in the underliquid), which corresponds to experiments. Nevertheless, we will show below that the underliquid can be obtained in such a way. For this purpose, it is necessary to perform the transition at the temperature $T \ll T_3$ and to create the conditions preventing the crystallization.

To substantiate this point, we consider the transitions gas–crystal (g-c) and gas–liquid (g-l) in more details. First, one needs to get the dependences $P(T)$ setting the curves g-c and g-l. As is known, along the line $P(T)$ of the phase transition the Clapeyron–Clausius relation should hold:

$$\frac{dP}{dT} = \frac{s_1(P,T) - s_2(P,T)}{v_1 - v_2}. \quad (30)$$

Let index 1 correspond to a gas, and index 2 to a liquid or a crystal. The data on the pressure of saturated vapors for He II [93] show that, at $T < \sim T_\lambda$, the temperature of a vapor is much larger than the temperature of the Bose condensation. Therefore, the vapor can be considered as an ideal gas. Assume that the vapors of other inert elements at $T \leq T_3$ can also be considered as an ideal gases. The entropy of a one-atom ideal gas consisting of atoms with zero spin and zero orbital moment (all inert elements, except for $H_2$) is known [94, 95]:

$$s_g = \frac{5}{2}k_B + k_B \ln\left[\left(\frac{k_B T}{P}\right)^{5/2}\left(\frac{m}{2\pi \hbar^2}\right)^{3/2}\right]. \quad (31)$$

Note that the first term in this formula is given in the literature with different coefficients: $3/2$ [95] and $5/2$ [94]. We did not study the reason for this difference and will use $5/2$ (for the estimates below, the difference between $5/2$ and $3/2$ is insignificant).

The entropy $s_2$ of a liquid or crystal at $T \leq T_3$ is determined mainly by the phonon contribution ($\sim T^3$), which is much less than the entropy $s_1 = s_g$ of a saturated vapor (we
remark that the Debye temperature for inert elements is comparable with $T_3$. The entropy of a Bose liquid at $T \to 0$ reads

$$s_l = \frac{2\pi^2 k_B}{45n} \left( \frac{k_B T}{\hbar c} \right)^3. \tag{32}$$

For $^4He$ atoms at $T = 1 \, K$ and at the pressure of saturated vapors $P \approx 1.6 \cdot 10^{-4} \, atm$, we get $s_g/s_l \simeq 3000$. For neon at the triple point, we have $P_3 = 0.427 \, atm$ and $s_g/s_l \simeq 7.7$. These estimates indicate that, in the region of temperatures from $0 \, K$ to $T_3$, the relation $s_l/s_c \ll s_g$ holds. In this case, $v_l/v_c \ll v_g$. Therefore, in the zero approximation, the curves gas-crystal and gas-liquid at $0 \leq T \leq T_3$ are given by the formula

$$dP/dT = \frac{s_g}{v_g} = \frac{Ps_g}{k_BT}. \tag{33}$$

Denote $\tilde{T} = T/T_3$, $\tilde{P} = P/P_3$. Then formula (31) can be written as

$$s_g/k_B = \frac{5}{2} \ln \tilde{T} - \ln \tilde{P} + s_3, \tag{34}$$

where $s_3$ is the value of $s_g/k_B$ at the triple point. Equation (33) takes the form

$$\frac{d\tilde{P}}{d\tilde{T}} = \frac{\tilde{P}}{\tilde{T}} \left( \frac{5}{2} \ln \tilde{T} - \ln \tilde{P} + s_3 \right). \tag{35}$$

Now, denote $y = \ln \tilde{P}$ and $x = \ln \tilde{T}$. Then Eq. (35) becomes

$$\frac{dy}{dx} = \frac{5}{2} x - y + s_3. \tag{36}$$

We need to find a solution satisfying the boundary condition $y = x = 0$ (for the triple point). The solution can be sought as a series $y = a_1 x + a_2 x^2 + \ldots + a_j x^j + \ldots$. After the simple transformations, we get

$$y = \xi + \frac{5x^2}{2} - \xi e^{-x}, \quad \xi = s_3 - \frac{5}{2}. \tag{37}$$

From (37) we obtain $P(T)$ for a saturated vapor at $0 < T \leq T_3$:

$$\tilde{P} = e^{\xi \tilde{T}^{5/2} e^{-\xi/\tilde{T}}}. \tag{38}$$

This is a solution in the zero approximation. It holds for both curves g-l and g-c. We do not know whether this solution was obtained previously.

$^4He$ has no triple point. If we set formally $T_3 = 1 \, K$ for $^4He$, then Eq. (38) agrees very well with the experimental pressure $P(T)$ of saturated vapors of $^4He$ at $T \leq 1 \, K$. If we take $T_3 = 3 \, K$, then Eq. (38) describes experiments only qualitatively (perhaps because formula (33) becomes a poor approximation for (30)). For Ne, Ar, Kr, and Xe, the dependence $P(T)$ for the sublimation curve was measured for temperatures $T \simeq (2/3 \div 1)T_3$. In particular, the experimental dependence $P(T)$ for neon at $T = 16 - 24 \, K$ is described by the fitting formula $\lg \tilde{P} \approx 3.2 - 21.39 \lg \tilde{T} + 5.4T - 8.6/T$. The approximate solution (38) with $\xi$ for neon ($\xi = 9.69$) gives the values of $\lg \tilde{P}$ less by about 10%.
Solution (38) was found by neglecting the corrections $s_2$ and $v_2$ in (30). At $\tilde{T} \ll 1$ these corrections are negligible. They increase with $\tilde{T}$, but remain small even at $\tilde{T} = 1$. In order to estimate the influence of corrections on the solution, we take the entropy $s_2/k_B = 4\tilde{T}^3 - (f + 1)\tilde{T}^f$ with $f > 3$ into account in (30). Here, the first term describes $s_2/k_B$ proper (for comparison, $s_l/k_B = 1.58\tilde{T}^3$ for neon at $\tilde{T} \ll 1$; while estimating $s_l$, we take $c_s(T \leq T_3) = c_s(T_3)$ and $\rho(T \leq T_3) = \rho(T_3)$). The second term effectively describes $v_2$ from the denominator. In this case, we get the solution

$$y = \xi + \frac{5x}{2} - \xi e^{-x} + e^{3x} - e^{f_x},$$

$$(39)$$

$$\tilde{P} = e^{\xi \tilde{T}^{5/2}} e^{-\xi/\tilde{T}} e^{\tilde{T}^3 - \tilde{T}^f}.$$  

$$(40)$$

In Fig. 2, this solution is shown as the curve g-l and solution (38) as the curve g-c. Of course, such correspondence between the formulae and the curves is only qualitative. For Fig. 2 we use parameter $\xi = 9.69$ corresponding to neon. In this case, the parameter $f = 7$ is chosen so that curve (40) lies above curve (38), and the slope of curve (40) at $T \to T_3$ is less than that of curve (38). As a result, curves (38) and (40) are similar to experimental curves g-c and g-l, respectively. The exact curves g-l and g-c can significantly differ from those presented in Fig. 2, because the corrections $s_2$ and $v_2$ were taken into account in a rough model form. However, this analysis is sufficient to show that the solutions of such type correctly describe experimental curves g-l and g-c. The second important conclusion is that though the corrections $s_2$ and $v_2$ separate the curves g-l and g-c, these curves should be close. For example, at $\tilde{T} = 0.1$ we have $P_{gl}/P_{gc} = e^{\tilde{T}^3 - \tilde{T}^f} \approx 1.001$, according to relations (38) and (40) with $f = 7$.

It is significant that, for inert elements, the slopes of the experimental $P(T)$ curves g-l (at $T > T_3$) and g-c (at $T < T_3$) near the triple point are very close [89]. This agrees with our conclusion that these curves should be close at $T \leq T_3$.

If the ratio $P_{gl}/P_{gc} = \zeta$ is close to 1, the phase transitions gas–crystal and gas–liquid are “switched-on” almost simultaneously. At the compression, the system transits in a liquid or a crystal depending on that which nuclei are generated faster: microdrops or microcrystals. In Appendix 4, where the formation of nuclei is considered, we will show that it is necessary to increase the pressure of a gas up to $P \approx P_{gc}^{1 + \phi/\phi}$ in order that the microdrops are generated faster, than microcrystals ($\phi$ depends on the substance; the characteristic value is $\phi \simeq 0.1$). If we use a vessel with smooth walls whose microstructure differs significantly from that of crystal nuclei, and if a gas is purified from impurities, then the formation of crystal nuclei should be suppressed, though the curve $P_{gc}(T)$ lies below the curve $P_{gl}(T)$ (see Appendix 4). Let the gas be compressed at the pressure $P \approx P_{gc}^{1 + \phi/\phi} \sim P_{gc}^{11} \sim 1.01P_{gc}$ (for $\zeta = 1.001$, according to the above estimate). Then one can expect that the gas will be condensed into a liquid. If the energy of this liquid $E^l(T, P) < E^c_0(P)$, then such underliquid will not crystallize. Of course, our estimates are crude, and exact formulae can give a much larger
ratio $P/P_{gc}$. However, we expect that $\zeta \sim 2$, i.e., the pressure $P$ should be increased by at least several times as compared with $P_{gc}$, in order that the spontaneous (bulk or surface) condensation of a gas into a liquid to begin.

According to the analysis in Appendix 4, in order to prevent the crystallization of a gas and to “switch-on” the bulk spontaneous mechanism of formation of nuclei, one needs to purify a gas from suspended solid impurities and to prevent the formation of crystalline nuclei on the walls. To achieve the latter, one can take a vessel with smooth walls (though, it is impossible to obtain an ideally smooth walls), and the molecules of walls should weakly interact with the molecules of a gas (or the crystalline ordering of walls should significantly differ from that of crystal nuclei forming from a gas). In addition, the molecular dynamics simulations show that the crystallization of a liquid on walls is suppressed, if the walls are covered with a solid amorphous layer whose structure is similar to that of a liquid \[97\] (see also \[98\], Sect. 2.4.2). We propose one more method: One can cover the walls from inside by a microscopically thin film of He II, then the surface of walls should be liquid and smooth. In this case, the formation of crystal nuclei on the walls would become difficult. Moreover, the interaction of helium atoms with molecules of the majority of gases is weak, which must prevent the adsorption of molecules of a gas on the walls and the formation of surface nuclei. It is noted in books \[99, 100\] that, at the compression of a gas at a temperature $T < T_3$, the metastable liquid is sometimes formed and then crystallizes. These properties are evidence of the validity of the inequality $E_0^c(P) < E_0^l(P)$ \[26\]. However, our analysis shows that, for some substances, the inequality $E_0^c(P) > E_0^l(P)$ \[25\] should hold. In this case, the liquid formed at the compression of a gas should be stable and should not crystallize.

Interestingly, the transition crystal–underliquid can occur at a negative pressure. By \[28\], we have $P_{ul-c}(T = 0) < 0$ for $v_l - v_c > 0$, $E_0^c(P) - E_0^l(P) < 0$ or for $v_l - v_c < 0$, $E_0^c(P) - E_0^l(P) > 0$. We may expect that $P_{ul-c}(T = 0) \sim -(100 \div 1000) \text{ atm}$. In this case, the state of underliquid can apparently be obtained by creating a negative pressure in a crystal. The idea of the creation of a liquid from a crystal by applying a negative pressure was advanced by J. Frenkel \[100, 101\].

The above analysis shows that the form of the $(P,T)$-diagram at low $P$ and $T$ should depend on how we got in this region. If we have got into it from above (by cooling a crystal), we obtain an ordinary diagram with the triple point. The result will be the same, if we will try to get into the region of underliquid from the bottom (from the region of a gas) or from the right (from the region of a liquid) in the absence of the conditions preventing the formation of crystal nuclei. But if we try to enter from the bottom (or from the right) in the presence of such conditions, then we should obtain the state of underliquid. In other words, the phase diagram in the region to the left from the melting curve and above the sublimation curve should have two levels (or two “layers”): liquid-type and crystal-type ones. Such liquid states were obtained previously by supercooling a liquid. In this case, it was considered in
the literature that the liquid state at \( T = 0 \) is impossible. Therefore, the supercooling of a liquid down to \( T \approx 0 \) and the obtaining of a stable liquid by the compression of a gas at \( T \approx 0 \) were also considered impossible. However, both are possible, since a liquid can have the zero temperature, as was shown in Sect. 2.

Our reasoning is general and should be suitable for any inert element (\( \text{H}_2 \), \( \text{Ne} \), \( \text{Ar} \), etc., see review [102]), except for helium. We propose to carry out three following experiments. (i) To supercool isobarically liquid \( \text{H}_2 \), \( \text{Ne} \), and \( \text{Ar} \) down to temperatures that are by several times less than the temperature of the Bose condensation of the ideal gas \( T_c = \frac{3.31}{(2s+1)^{2/3}} \frac{\hbar^2 m}{k_B n^{2/3}} [94] \) (here, \( s \) is the spin of a particle; for liquid inert elements, except for hydrogen and helium, \( T_c < 1 \text{ K} \)). In this case, we should obtain a superfluid underliquid. We note that, at a strong overcooling, the energy barrier of the nucleation for some liquids, apparently, disappears (see [98], Sect. 1.1.4 and 2.2.2). Such liquids can easily crystallize spontaneously. One needs to pass through this temperature region and to get lower \( T < \sim T_c \) at which the microcrystals should become unstable (according to the above analysis). (ii) To compress isothermally a dilute gas (\( \text{H}_2 \), \( \text{Ne} \), \( \text{Ar} \)) at \( T \sim 0.1T_3 \) up to a pressure that exceeds by several times the saturated vapor pressure for the same \( T \). The underliquid should also be created. In both experiments, it is necessary to create the conditions hampering the crystallization (see the discussion above and Appendix 4), and condition (25) must be satisfied for the stability of a liquid. In the second experiment, a less supersaturation is required. Therefore, the requirements to the purification and to walls can be apparently less strict. (iii) To create a negative pressure \( P_{ul-c} \lesssim -1000 \text{ atm} \) in a crystalline inert element at \( T \lesssim 0.1T_3 \). One can expect that some of such crystals will melt into an underliquid.

If the underliquid is metastable (inequality (26)) and has a small life-time, then such underliquid state can be unobservable. However, \( \text{^4He} \) is stable (inequality (25)). Therefore, it is natural to expect that, among inert elements, there are several other ones with the stable underliquid state. In view of this, it is desirable to execute the experiments with all inert elements (except for \( \text{^4He} \)).

The inert elements were investigated mainly at \( T > T_3 \). The number of experiments at \( T \ll T_3 \) is much less. In the last ones the crystals, being in equilibrium with their vapors, were studied at \( T \geq 1 \text{ K} \) [90, 96]. We assume that the underliquid state was not obtained earlier because the conditions hampering the crystallization were not created. Therefore, a gas or liquid turned into a crystal, rather than into an underliquid. Moreover, the underliquid state was considered impossible and was not sought.

Why do the liquids in the Nature crystallize at the cooling, though the crystal corresponds to a highly excited state of a system? Mathematically, this is related to the fulfillment of condition (27) for the liquid–crystal transition. The possible physical explanation is as follows: at the cooling of a liquid down to some temperature, the microcrystals arising as fluctuations become stable. And the visual reason is that the system falls into the local energy minimum.
corresponding to a crystal (see Fig. 1). As a result, the liquid crystallizes, and we obtain a crystal with some number of quasiparticles. In this case, the cooling of the crystal means a decrease in the number of quasiparticles introduced relative to GS of a crystal.

We note also that, at the strong supercooling, the viscosity of some liquids increases sharply, and they transit into a glass-like state. However, the atoms of inert gases are spherically symmetric (except for hydrogen which forms molecules $H_2$) and, therefore, should not turn into a glass at the supercooling. We may expect that, at $T \ll 0.1T_c$, liquid inert elements have to be similar to He II, i.e., they should contain a condensate of atoms with zero momentum and should be superfluid.

Undoubtedly, inequality (24) should be correct. Therefore, the region of underliquid must exist, and the task is to enter this region in experiments.

In Appendix 3, we also consider the third principle of thermodynamics and properties of $^4$He.

4 Conclusions

Our analysis shows that the genuine ground state of a system of spinless bosons should correspond to a liquid or gas, at any density. We have proved this for an infinite 3D system and a finite ball-shaped 3D one. It is natural to expect that this assertion is valid for finite systems of any shape. In this case, the lowest states of a liquid and a crystal must satisfy the inequality $E_c^0(P) > E_l^0(P)$ (25) or $E_c^0(P) < E_l^0(P)$ (26). If inequality (26) holds, the stable state of the system at $T \to 0$ is a crystal, that corresponds to the available experimental data. However, we expect that relation (25) holds for the majority of inert elements (in particular, it holds for $^4$He). The underliquid state, that does not crystallize at the cooling and is superfluid at very low temperatures, should exist for such substances. This is our main experimental prediction. We assume that the underliquid can be created in experiments by compressing a gas at a low temperature or by strong supercooling an ordinary liquid (in both cases, it is necessary to create the conditions preventing the crystallization).

According to the above analysis, a Bose crystal is a standing wave in the probability field. Most likely, this property is a general principle valid not only for Bose systems. Therefore, it is possible that the underliquid state and the superfluidity are inherent not only in inert elements. Such properties can be inherent in all substances that form molecular crystals: inert elements, water, methane, etc. Although it may seem implausible now.

If inequality (24) is true under any boundary conditions, it will change our comprehension of the nature of crystals and lead to the discovery of new physical phenomena. For example, the space apparatus “New Horizons” found in 2015 that the Sputnik Planitia surface on Pluto consists of solid nitrogen and is similar to a mosaic made of hexagons and pentagons. This...

\footnote{Such idea was proposed previously in \cite{72}, but that work of ours is immature and contains something very similar to errors; see, in particular, the Introduction in \cite{80}}
valley has no craters, though they are present on the remaining Pluto’s surface. It is possible that a liquid water ocean exists under the surface. That is surprising because the Pluto’s surface temperature is about 40 K. However, we have established above that the liquids of low viscosity can exist even at \( T = 0 \) K. This can help one to understand some anomalous properties of cosmic objects.

We hope that the above-proposed experiments to create the underliquid state will be carried out.

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5 Appendix 1. Wave functions of a many-particle Bose system in the momentum approach

We now determine the general form of WF of the ground state and any excited state of a periodic Bose system on the basis of the analysis in [39]. Since work [39] is not widely available, we give below the derivation of these formulae. Consider the functions

\[
\psi_f^0 = c_{00},
\]

\[
\psi_f^{k_1} = c_{11} \rho - k_1,
\]

\[
\psi_f^{k_1,k_2} = c_{22} \left( \rho - k_1 \rho - k_2 - \frac{\rho - k_1 - k_2}{\sqrt{N}} \right),
\]

\[
\psi_f^{k_1,k_2,k_3} = c_{33} \left( \rho - k_1 \rho - k_2 \rho - k_3 - \frac{1}{\sqrt{N}} \left( \rho - k_1 \rho - k_2 - k_3 + \rho - k_2 \rho - k_1 - k_3 + \rho - k_3 \rho - k_1 - k_2 \right) + \right. 
\]

\[
\left. + \frac{2}{N} \rho - k_1 - k_2 - k_3 \right),
\]

\[
\psi_f^{k_1\ldots k_N} = c_{N1} \rho - k_1 \cdots \rho - k_N + c_{N2} \sum_{P(k_j)} \rho - k_1 \cdots \rho - k_{N-2} \rho - k_{N-1} - k_N + 
\]

\[
+ \cdots + c_{NN} \rho - k_1 - \cdots - k_N,
\]

where \( c_{ij} \) are constants, and \( \sum_{P(k_j)} \) is the sum over all permutations of the vectors \( k_j \). These are the wave functions of a periodic system of \( N \) free spinless bosons. Here, \( \psi_f^0 \) corresponds to the ground state; \( \psi_f^{k_1} \) describes the state, where one boson has a momentum \( \hbar k_1 \), and \( N - 1 \) bosons have the momentum 0; and so on; \( \psi_f^{k_1\ldots k_N} \) describes the state in which each of the bosons has some nonzero momentum \( \hbar k_j \). These functions are solutions of the Schrödinger equation with the given BCs, and, therefore, form the complete orthonormalized set of basis functions. Any Bose-symmetric WF of the variables \( r_1, \ldots, r_N \) for the Schrödinger problem with interatomic interaction and periodic BCs can be expanded in this basis. This
is the ground for the theory of quantum liquids constructed in [39, 61]. Hence, any WF
\( \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) \), being an eigenfunction of the momentum operator of the system of \( N \) identical bosons and corresponding to the momentum \( \hbar \mathbf{p} \), can be presented in the form of a sum

\[
\Psi_\mathbf{p} = a_1 \psi_\mathbf{p}^f + \sum_{k_1, k_2} a_2(k_1, k_2) \psi_\mathbf{k}_1 \mathbf{k}_2 + \ldots + \sum_{k_1 \ldots k_N} a_N(k_1, \ldots, k_N) \psi_\mathbf{k}_1 \ldots \mathbf{k}_N. \tag{47}
\]

Using Eqs. (41)–(46), this expansion can be written as

\[
\Psi_\mathbf{p} = b_1(\mathbf{p}) \rho_\mathbf{p} - \rho_\mathbf{p} + \sum_{q_1 \neq 0} b_2(q_1; \mathbf{p}) \frac{2^q q!}{2! \sqrt{\pi}} \rho_{q_1} \rho_{-q_1} + \ldots + \sum_{q_1, q_2 \neq 0} b_N(q_1, \ldots, q_{N-1}; \mathbf{p}) \frac{N!}{N! \sqrt{\pi}} \rho_{q_1} \ldots \rho_{q_N} \rho_{-q_1} \ldots - \rho_{q_{N-1}}. \tag{48}
\]

Here, the wave vectors \( \mathbf{k}_1, \mathbf{q}_1, \mathbf{p}_1, \mathbf{p} \) are quantized by the law (for 3D) \( \mathbf{q} = 2\pi (j_x/L_x, j_y/L_y, j_z/L_z) \), where \( j_x, j_y, j_z \) are integers, and \( L_x, L_y, L_z \) are the system sizes.

If GS is non-degenerate, then the wave function of GS is always positive and corresponds to zero momentum (as was shown in Sect. 2). Therefore, it can be presented in the form \( \Psi_0 = C \cdot e^{S_0} \), where \( S_0 \) is \( \Psi_\mathbf{p} \) (18) with \( \mathbf{p} = 0 \) [39, 65]:

\[
S_0 = \sum_{q_1 \neq 0} \frac{a_2(q_1)}{2!} \rho_{q_1} \rho_{-q_1} + \sum_{q_1, q_2 \neq 0} \frac{a_3(q_1, q_2)}{3! \sqrt{\pi}} \rho_{q_1} \rho_{q_2} \rho_{-q_1} - q_2 + \ldots + \sum_{q_1, \ldots, q_{N-1} \neq 0} \frac{a_N(q_1, \ldots, q_{N-1})}{N! \sqrt{\pi}} \rho_{q_1} \ldots \rho_{q_N} \rho_{-q_1} \ldots - q_{N-1}. \tag{49}
\]

In this case, the constant \( b_1(0) \rho_0 \equiv \sqrt{N} b_1(0) \) is taken into account in \( C \). If each of the functions \( S_j \) from \( S_0 \) is expanded in a Fourier series in \( j - 1 \) variables, then the resulting series can be written in the form \( S_0 + const \) with \( S_0 \) (49). For example, the following equality holds:

\[
\frac{1}{3!} \sum_{j_1 \neq j_2, j_3, j_3} \tilde{S}_3(\mathbf{r}_{j_1} - \mathbf{r}_{j_2}, \mathbf{r}_{j_2} - \mathbf{r}_{j_3}) = \sum_{q_1, q_2 \neq 0} \frac{\tilde{a}_3(q_1, q_2)}{3! \sqrt{\pi}} \rho_{q_1} \rho_{q_2} \rho_{-q_1} - q_2 + \frac{1}{2!} \sum_{j_1, j_2} g_2(q_1) \rho_{q_1} \rho_{-q_1} + \frac{1}{2!} \sum_{j_1, j_2} \tilde{S}_2(\mathbf{r}_{j_1} - \mathbf{r}_{j_2}) + const. \tag{50}
\]

The functions \( \tilde{a}_3(q_1, q_2), g_2(q_1) \), and \( \tilde{S}_2(\mathbf{r}_{j_1} - \mathbf{r}_{j_2}) \) can be easily determined, by expanding \( S_3(\mathbf{r}_{j_1} - \mathbf{r}_{j_2}, \mathbf{r}_{j_2} - \mathbf{r}_{j_3}) \) in a Fourier series in the variables \( \mathbf{r}_{j_1} - \mathbf{r}_{j_2}, \mathbf{r}_{j_2} - \mathbf{r}_{j_3} \) and making simple transformations. This proves that if GS is non-degenerate and \( \ln \Psi_0 \) can be expanded in a Fourier series, then \( \ln \Psi_0 = S_0 + const \), where \( S_0 \) has the form (49) or the equivalent form (41).

Formula (48) can be written in the form (18), (19) (with other \( b_j \)), which is more suitable for the description of quasiparticles.
We note that function (49) can be isotropic (formula (4)) or anisotropic (formula (7)). The above analysis (in this appendix) does not allow us to establish whether \( S_0 \) (49) is isotropic. However, it was shown in book [47] (see Appendix 2 below) that GS of a Bose system is non-degenerate. Moreover, we have shown in Section 2 that any anisotropic state of the infinite 3D Bose system is degenerate. This property establishes a restriction for \( S_0 \): for the infinite 3D Bose system, this function must be isotropic, since it corresponds to the ground state. Such function can depend only on the quantities that are invariable at any rotation, as well as at any translations.

Therefore, we can write \( S_0 \) in the form
\[
S_0 = S_0(f_1, \ldots, f_j),
\]
where
\[
f_l = (r_{j_1} - r_{j_2})^2, (r_{j_1} - r_{j_2})(r_{j_2} - r_{j_4}), \text{ or } (r_{j_1} - r_{j_2})(r_{j_3} - r_{j_4}).
\]
It can be proved directly that such \( S_0 \) satisfies the equality
\[
\hat{L}S_0(r_1, \ldots, r_N) = 0
\]
for all \( N \geq 2 \). Here, \( \hat{L} \) is the operator of total angular momentum of a system of \( N \) particles:
\[
\hat{L} = \sum_{j=1}^{N} [r_j \times \hat{p}_j] = -i\hbar \sum_{j=1}^{N} \left[ r_j \times \frac{\partial}{\partial r_j} \right].
\]
It is natural to expect that, at the transition to a finite periodic system, the structure of \( S_0 \) does not change. Hence, for a finite periodic 3D system, \( S_0 \) should also be isotropic. Thus, function (6), (4) specifies the general form of GS WF of a periodic 3D Bose system.

6 Appendix 2. Proof of the nondegeneracy of the ground state

In the classical monograph by R. Courant and D. Hilbert [47], the theorem of nodes was proved for one particle located in a finite two-dimensional volume with zero BCs. The proof can be easily generalized to the case of a large number of particles and any dimensionality of space. The proof in [47] admits the presence of the degeneracy (\( E_j = E_{j-1} \)) of finite multiplicity (multiplicity is finite, if the volume of the system is finite, see [47], §2). If GS is doubly degenerate, then one of the states is described by a nodeless WF \( \psi_1 \) (according to the theorem of nodes). WF \( \psi_2 \) of the second state can have a single node, according to the same theorem. On the other hand, \( \psi_2 \) should be orthogonal to \( \psi_1 \) and, therefore, must have at least one node. Thus, the theorem of nodes [47] admits the possibility for GS to be degenerate.

The nondegeneracy of GS was proved at the other place of book [47]. The proof is based on the Jacobi method (see [47], §7). We will give it in a slightly more detailed form.

Consider the Schrödinger equation
\[
-\Delta \psi + U(x,y)\psi - E\psi = 0
\]
for one particle located in a 2D region \( G = (x,y) \) with the zero BCs (\( \psi(x,y) = 0 \) on the boundary of the region \( G \)). Here, \( U(x,y) \) is a potential, and we set \( \hbar = 2m = 1 \). If there
exists a solution $\psi_1$ of Eq. (53) corresponding to the smallest eigenvalue $E_1$, then $\psi_1$ can be found by solving the following variation problem [17]: the inequality

$$D[\varphi] = \int_G dxdy(\varphi_x^2 + \varphi_y^2 + U\varphi^2) \geq E_1 \int_G dxdy\varphi^2$$

(54)

should be satisfied for all functions $\varphi(x,y)$ that are equal to zero on the boundary of the region $G$ and have “good” properties ($\varphi$ should be continuous, whereas $\varphi_x$ and $\varphi_y$ should be piecewise continuous). Here, $\varphi_x \equiv \partial\varphi/\partial x$, $\varphi_y \equiv \partial\varphi/\partial y$. Inequality (54) becomes an equality only for $\varphi(x,y) = c_1\psi_1(x,y)$, where $c_1 = \text{const}$. It follows from the theorem of nodes that $\psi_1$ has no nodes [17].

Assume that GS is degenerate and corresponds to two functions: $\psi_1$ and $\psi_2$. In this case, $\psi_1$ has no nodes, and $\psi_2$ must have one node (as was noted above). In this case from the variation viewpoint, $\psi_1$ and $\psi_2$ satisfy condition (54) and the zero BCs, and $\psi_2$ satisfies additionally the condition of orthogonality of the functions $\psi_1$ and $\psi_2$. Since $\psi_1$ has a constant sign everywhere inside $G$, we may set $\psi_2(x,y) = \vartheta(x,y)\psi_1(x,y)$. We will see now whether such solution is possible. We set $\varphi(x,y) = \eta(x,y)\psi_1(x,y)$ in $D[\varphi]$ (51). Then

$$D[\varphi] = \int_G dxdy[\psi_1^2(\eta_x^2 + \eta_y^2) + \eta^2(\psi_{1x}^2 + \psi_{1y}^2) + 2\psi_1\psi_1x\eta x + 2\psi_1\psi_1y\eta y + U\eta^2\psi_1^2].$$

(55)

Let us use the relations $2\eta x = (\eta^2)_x$, $2\eta y = (\eta^2)_y$ and integrate the terms with $\eta x$ and $\eta y$ by parts. We obtain two integrals over the boundary which are equal to zero due to the zero BCs. The remaining terms give

$$D[\varphi] = \int_G dxdy[\psi_1^2(\eta_x^2 + \eta_y^2) - \eta^2\psi_1\Delta\psi_1 + U\eta^2\psi_1^2].$$

(56)

Since $\psi_1$ satisfies Eq. (53) with $E = E_1$, formula (56) is reduced to

$$D[\varphi] = \int_G dxdy[\psi_1^2(\eta_x^2 + \eta_y^2) + E_1\eta^2\psi_1^2] \geq E_1 \int_G dxdy\varphi^2.$$  

(57)

The equality is obtained only for $\eta(x,y) = C = \text{const}$. Hence, the wave function corresponding to the energy $E_1$ can have only the form $\text{const} \cdot \psi_1(x,y)$. Therefore, the solution $\psi_2(x,y) = \vartheta(x,y)\psi_1(x,y)$ with $\vartheta(x,y) \neq \text{const}$ is impossible. This proves that the lowest level is always non-degenerate. In this case, any excited state $\psi_{j>1}(x,y)$ can be degenerate (because $\psi_{j>1}(x,y)$ has nodes, and, therefore, the representation $\varphi(x,y) = \eta(x,y)\psi_j(x,y)$ is inapplicable).

If we pass in all formulae from $x,y$ to $r_1, \ldots, r_N$, the reasoning conserves its validity. Therefore, the conclusion about the nondegeneracy of GS is true for systems with any $N$ and for any dimensionality of space. The above analysis was performed for a finite system under the zero BCs. We may expect that the main conclusion holds for any BCs and for infinite systems. Apparently, the above consideration can be applied to infinite systems, if the zero BCs are set at infinity.
Appendix 3. The third law of thermodynamics, properties of $^4$He, Monte Carlo simulations

We now consider the third principle of thermodynamics. Some researchers believe that namely a crystal (rather than a liquid) corresponds to the genuine GS of a system, since the crystal is more ordered in the $r$-space and, therefore, should be characterized by a lower entropy. However, we have seen in Sect. 2 that in point of fact a liquid is characterized by a higher symmetry as compared with a crystal. Moreover, according to quantum statistics, the entropy is determined by properties of a system in the space of quantum states (not in the $r$-space). It is given by the formula $S = k_B \ln(N(E))$ [95], where $N(E)$ is the number of states with energy close to $E$. To what is $N(E)$ equal for the GS of a Bose crystal? Inequality [24] implies that many liquid states with energy close to $E_c$ must exist. If we take them into account, we get $N(E_c) \gg 1$ and $S \neq 0$. Therefore, it is necessary to introduce the natural postulate: in the calculations of thermodynamic quantities, one needs to take only states of the phase under consideration (gas, liquid, or crystal) into account in the statistical sum. In addition, the complete set of eigenfunctions of the Hamiltonian should contain the solutions for crystal lattices of various types and various spatial orientations (see Subsect. 2.2). Of course, while describing a crystal, it is necessary to consider in the statistical sum only the states associated with one type and one orientation of the lattice. Then for each phase we obtain $N(E) = 1$ and $S = 0$ at $T = 0$, i.e., the Nernst theorem is satisfied. However, if the lowest state of a real finite crystal is $j$-fold degenerate, we obtain for it $S(T = 0) = k_B \ln(j)$.

$^4$He has particular properties. According to experiments, liquid $^4$He (He II) at $P \approx 25 \text{ atm}$ and $T \lesssim 0.8 \text{ K}$ solidifies and transforms into a hcp crystal [9]. In this case, for liquid and solid $^4$He, we have, respectively, $E'_0 \approx -6.6 \text{ K}$ [106, 107] and $E'^c_0 \approx -5.96 \text{ K}$ [108]. That is, the GS energy of a crystal by $0.6 \text{ K}$ higher, than $E_0$ of a liquid. In this case, liquid and solid helium have densities of $0.1725 \text{ g/cm}^3$ [106, 109] and $0.191 \text{ g/cm}^3$ [108, 109], respectively. To verify the basic inequality (24), we need to compare $E_0$ of liquid and solid helium at the same $\rho$. We can determine $E_0$ of liquid helium at $\rho = 0.191 \text{ g/cm}^3$ by the known formula in [106, 107]. In this case, one needs to know $P(\rho)$ of He II at $\rho = 0.1725-0.191 \text{ g/cm}^3$. However, such data are not available, since He II does not exist at such densities: it solidifies. It is significant that GS of liquid helium at the crystallization pressure ($P \approx 25 \text{ atm}$) has a lower energy, than GS of a crystal. Nevertheless, liquid helium crystallizes. The reason is known and is as follows. $^4$He possesses large zero oscillations. Therefore, at low pressures, the crystal is unstable. As a result, the system at low pressures and temperatures is in the state of underliquid. This is He II. As the pressure increases, the ratio of the amplitude of zero oscillations to the lattice period decreases [9, 110]. At $P \gtrsim 25 \text{ atm}$, the crystal embryos become stable and liquid $^4$He crystallizes [111, 112]. In this case, the formation of microcrystals and the external pressure make the liquid state unstable: the external pressure compresses the system, performs the work, and increases the energy of the system up to $E_0$. 
of a crystal. This results in the formation of a crystal. By such a scenario, the ground state of $^4\text{He}$ at $P > 25 \text{ atm}$ corresponds to a liquid, but this state cannot be obtained. However, the crystallization pressure should rise above $25 \text{ atm}$ provided we prevent the formation of crystal nuclei (one needs to purify helium from impurities and use the smooth walls with a microstructure different from the structure of a helium crystal). We do not know whether attempts to obtain high-density liquid helium in this way were made before. If He II with $\rho = 0.1725–0.191 \text{ g/cm}^3$ could be obtained, it would be possible to verify inequality (24) for $\rho = 0.191 \text{ g/cm}^3$.

The analytic analysis of crystalline solutions is very complicated. Therefore, the majority of theoretical studies of quantum crystals were executed numerically by the Monte Carlo (MC) method (see works [7, 8, 21, 22, 33, 40, 48, 49, 50, 55, 113, 114, 115, 116, 117, 118, 119, 120, 121, 122, 123] and reviews [11, 35, 36, 124]; an introduction to the MC methods can be found in books [125, 126]). Some MC methods are “exact” and are independent of (by authors’ opinion) a trial function [8, 21, 22, 114, 116], the inequality $E_0^c(\rho) < E_0^l(\rho)$ [7, 113], a sharp turn on the curve $\langle r^{-12} \rangle(a_1)$ (a_1 is the parameter of the Bijl–Jastrow WF) [33], and a jump of $\rho$ [120, 127]. The basic property allowing one to separate a quantum crystal from a liquid, namely, the anisotropy of solutions, was studied only in a few works [40, 50, 114, 118, 121, 122, 123] (solutions for the classical system of hard balls see in [128]).

By means of the symmetry analysis we have shown in Sect. 2 that the genuine GS must correspond to a liquid for any density. The symmetry analysis is a more strong argument, than a MC simulation. Since the former presents the exact information, whereas the latter gives only an approximate one. Therefore, we suppose that the MC simulations gave always a nodeless liquid solution or a crystalline solution corresponding to a WF with nodes (instead of a nodeless crystalline solution). In particular, the isotropic function $g_2(\mathbf{r}_1 - \mathbf{r}_2)$ was obtained for a crystalline solution [114]. The authors of work [114] interpreted such solution as a crystalline one, only because it corresponds to the densities at which the natural helium is a solid substance. As for the isotropy, they related it to large zero oscillations [114]. In our opinion, the isotropy of $g_2(\mathbf{r}_1 - \mathbf{r}_2)$ indicates clearly the liquid character of the solution. With the help of the shadow PIGS (path integral ground state) MC method, the authors of work [118] obtained a crystal-like distribution of atoms. Within an analogous method the solutions for 2D and 3D crystals were obtained in [50] and [40], respectively. The crystal character of a solution was determined by the Bragg peak of the structural factor $S(k_y)$ [50] or $S(k)$ [40]. We think that works [40, 50, 118, 121, 122, 123] present the crystalline
solutions corresponding to a local crystalline energy minimum (see Fig. 1) and WFs with nodes. As far as we understand, the Green’s function MC [114, 116], PIGS MC [40, 50, 118], PIMC [121, 122], and a diffusion MC [123] are “exact” methods, but they do not allow one to reliably clarify whether the obtained WF has nodes. In works [40, 50], no comparison of the parameters of the Bragg peak and the lattice parameters was made. It is worth to verify whether the lattice is one-dimensional (this would explain the smallness of the quantity $|E_0^l - E_0^c| \sim (0.001 \div 0.01)|E_0^l|$ [8, 50]; indeed, the 1D lattice corresponds to WF with a small number of nodes; therefore, the energy has to be close to the energy of a nodeless liquid solution). On the other hand, a small value of $|E_0^l - E_0^c|$ can be connected with the Yukawa potential [8].

Usually, the MC simulations lead to the crystalline solution at a sufficiently high concentration $n$. This is apparently because an increase in many-particle corrections in (4) with $n$ [39, 74]. In this case, the trial two-particle function $\Psi_0$ deviates more and more from the exact one. Therefore, the difference between the trial $E_0$ and the exact one can exceed the exact difference $|E_0^l - E_0^c|$. As a result, the method can lead to the crystalline minimum region (Fig. 1). If the system falls in the crystalline minimum in the process of simulation, one can try to take it off this minimum by increasing the step of simulation by one order of magnitude or by starting a new simulation with a small step using the previous or new trial function. The “exact” MC simulations usually give information that is insufficient to reliably determine the lattice type and to clarify whether the crystal WF is nodeless. For the determination of a type and dimensionality of the lattice, one needs to find the function $g_2(r_1 - r_2)$ or $S(k)$. In this case, it is necessary to check $\Psi_0$ for nodes. We do not know whether this can be realized with a good accuracy at $N > 10$ (though the fixed-node MC methods allow one to determine, in principle, the node structure of WF at $N \gg 1$ [129]). We hope that the modern capabilities of computers and theory are sufficient to perform the detailed studies and to clarify the general picture with the help of MC simulations.

8 Appendix 4. Formation of nuclei

The theory of formation of nuclei of a new phase is not completed (especially, the theory of crystallization), but its general contours are apparently clear (see reviews [98, 130] and books [86, 99, 100, 131, 132, 133, 134, 135, 136, 137, 138]). The nuclei of the other phase can be created on the walls of a vessel and in bulk. We will consider only the simpler bulk case.

The bulk condensation of a gas into a crystal or liquid occurs under the avalanche-like increase in the number of nuclei of the new phase. Such growth is possible, if $P$ or $T$ differs from the value $P = P_\infty$ or $T = T_\infty$ corresponding to the condition of equilibrium (27). Consider a gas at low $P = P_\infty$ and low $T = T_\infty$. Let us compress it isothermally so that the pressure increases up to some $P > P_\infty$. In such gas, the embryos of the liquid phase (microdrops) and the crystalline one (microcrystals) should randomly appear. In a
supersaturated gas (vapor) at the pressure $P_r \geq P_\infty$, a droplet is in equilibrium with a gas, if its radius $r$ satisfies the Kelvin’s formula \[95, 100, 131\]:

$$P_r(T) = P_\infty(T) \exp \left( \frac{2\alpha_{lg}}{nk_BT} r \right),$$

(58)

where $n$ is the concentration of atoms in a droplet, $P_\infty$ is the saturated vapor pressure, $\alpha_{lg}$ is the coefficient of surface tension of a liquid on the boundary with a gas. Let the pressure $P_r$ correspond to the radius $r = r_0$, according to (58). Then the droplets of radius $r < r_0$ must evaporate. The condensation of atoms of a gas on a droplet decreases the pressure in a gas, which makes it possible for the droplets of radius $r > r_0$ to exist. As a result, the mean radius of droplets must increase with the time, until the whole gas transforms into one large drop \[95\]. The crystal embryos in a gas can be described analogously. We will get formula (58), where the parameters of a microdrop should be replaced by those of a microcrystal.

According to a more detailed theory, the process of formation of embryos is as follows \[100, 130, 131, 134, 135, 136, 137\]. The fluctuations in a gas result in the spontaneous formation of microscopic embryos of a liquid (microdrops) and a crystal (microcrystals) in a gas. The embryo can randomly capture atoms of the gas, which will lead to the growth of this embryo. The reverse process is possible as well. As a result, some (non-stationary, generally speaking) distribution of embryos over sizes should be formed. In this case, the embryos of sizes larger than the critical one (Eq. 58) must unboundedly grow. Such embryos are usually called nuclei. If the system is supplied with a gas in the amount compensating the loss due to the formation of nuclei, we get a stationary distribution of nuclei and the continuous transformation of small nuclei into large ones. If such pumping of a gas is absent, then in the usual case (isothermal formation of nuclei in a closed system with permanent supersaturation) the non-stationary process eventually becomes stationary \[136, 137, 138\]. Therefore, we may consider the process to be stationary. The kinetic analysis shows that, in this case, the rate $J$ of homogeneous (i.e., without exterior impurities) formation of nuclei is \[98, 99, 100, 131, 133, 134, 135, 136, 137, 138\]

$$J = n_g B e^{- \frac{W}{k_BT}},$$

(59)

where $n_g$ is the gas concentration, $B$ is the kinetic factor (which can depend on $P$ and $T$), $W > 0$ is the work of formation of a critical nucleus (an embryo of such size for which $W$ is maximum at the given $P$ and $T$). Condition (58) yields the radius of such a nucleus as a function of $P = P_r$ at $T = T_\infty = \text{const}$. Frequently, the dependence of the critical radius $r$ on $T$ at $P = P_\infty = \text{const}$ is studied. Then \[100, 134\]

$$r = \frac{2\alpha_{lg}T_\infty}{nq(T_\infty - T)},$$

(60)

where $n$ is the concentration of atoms in a nucleus, $q = T[s_g(P, T) - s_{l,c}(P, T)]$ is the latent heat of the phase transition per atom. As is seen, the higher the supercooling of a vapor, the less the nucleus radius.
It is difficult to calculate the value of $B$ in (59). Different models give different values. Within the classical approach (high $T$ and large nuclei), J. Gibbs [86] found $W$ for a critical liquid nucleus,

$$W_l = \varsigma \alpha_{lg}/3,$$

and for a critical crystal nucleus,

$$W_c = \sum_j \varsigma_j \alpha_j/3.$$

Here, $\varsigma = 4\pi r^2$ is the droplet surface area, $j$ is the number of a crystal face, $\varsigma_j$ is the area of the $j$-th face of a crystal, and $\alpha_j$ is the coefficient of surface tension for the $j$-th face of the crystal which contacts with the gas. It is useful to write formula (62) in the form [99]

$$W_c = \varsigma\bar{\alpha}_{cg}/3,$$

where $\bar{\alpha}_{cg}$ is the average coefficient of surface tension of the crystal on the boundary with the gas, and $\varsigma$ is the area of a sphere with the volume equal to that of a crystalline nucleus. At $T = T_\infty$ and $P = P_\infty$, the radius of a critical nucleus is $r = \infty$. Therefore, $J$ turns to zero, which corresponds to the equilibrium of phases.

Apparently, the underliquid can be obtained easier by means of the isothermal compression of a gas, than by its isobaric cooling. We now consider only the first way. The modern theory cannot exactly conclude whether the compressed gas will turn into a liquid or a crystal. This is not surprising, because the process of transition of one phase into another one is complex and depends on many factors.

First, we note that $W$ is less at the condensation of a gas on the surface, than at the condensation in bulk [130, 131, 132, 135, 137]. In particular, the work of formation of a dome-shaped critical nucleus (liquid or crystalline) of radius $r_0$ on a solid wall is [131, 132, 135, 138]

$$W^{2D} = (\varsigma \alpha/12)[2 + \cos \theta][1 - \cos \theta]^2,$$

where $\varsigma = 4\pi r_0^2$, $\theta$ is the angle between the nucleus surface and the wall, $\alpha$ is the surface tension of the nucleus that is in contact with a gas. At the complete nonwetting ($\theta = \pi$), the value of $W^{2D} = \varsigma \alpha/3$ coincides with that of the bulk work $W$ [61] or [63]. If the wetting is present ($\theta < \pi$), then $W^{2D} < W_l, W_c$, and a nucleus can be easier formed on the wall, than in bulk. Of course, crystallization is a complex process that is not reduced to the formation of dome-like nuclei. However, formula [64] shows that a crystal nucleus can be easier formed on the surface, than in bulk [99, 131, 134, 135, 137]. Therefore, if the gas contains solid impurities (or the walls of a vessel contain some inhomogeneities able to become the centers of condensation), then the surface condensation, rather than the bulk one, is realized. In practice, the impurities and inhomogeneities of walls are usually present. Moreover, $W^{2D}_l < W_l$ even for the ideally smooth wall provided $\theta < \pi$. Therefore, the condensation of a gas usually occurs on the walls or on impurity particles.
According to experiments, at $T < T_3$ a gas condenses into a crystal. This is because the gas-crystal curve lies below the gas-liquid one (see Fig. 2). Microscopically, this means that $W_{c}^{2D}$ corresponding to the formation of a two-dimensional critical crystal nucleus is less than the work $W_{l}^{2D}$ of the formation of an analogous liquid nucleus. The reason for this is that the crystalline structure of a substrate usually decreases $W_{c}^{2D}$ and thus stimulates the formation of namely crystalline nuclei. In particular, the condensation of a gas into a crystal becomes more intense, if a substrate on which the condensation occurs is a crystal of a close structure [130, 131, 133, 135, 137], because in this case $W_{c}^{2D}$ decreases.

In practice, the formation of crystal nuclei can be prevented if the gas is well purified from impurity particles and the vessel with very smooth walls is used. In addition, the microstructure of walls of a vessel should be significantly different from the microstructure of a crystal, into which the gas can condense. Under these conditions, the condensation of a gas into a liquid (on the walls or in bulk) should be dominant.

Assume that the bulk homogeneous mechanism of spontaneous formation of nuclei is realized. In this case, crystalline and liquid nuclei will arise. The rate of each of these processes is given by formula (59), where $W$ is determined by formulae (61) or (63). It is clear that $J_c \ll J_l$ at $T \to 0$ provided

$$\lambda \equiv \frac{W_c}{W_l} > 1.$$  \hspace{1cm} (65)

In this case, the condensation of a gas into droplets is more probable. Let us find the conditions under which relation (65) is satisfied. Formulae (58), (61), and (63) yield

$$\lambda = \frac{\bar{\alpha}_{cg}^3 n_l^2 \ln (P/P_{cg}^{\infty})^2}{\bar{\alpha}_{lg}^3 n_c^2 \ln (P/P_{lg}^{\infty})^2},$$  \hspace{1cm} (66)

where $n_l$ and $n_c$ are the concentrations of atoms in a microdrop and a microcrystal, respectively, at the same pressure $P$. We set $P_{lg}^{\infty} = \zeta \cdot P_{cg}^{\infty}$, $\bar{\alpha}_{cg} = (1 + \eta)\bar{\alpha}_{lg}$, $n_c = (1 + \vartheta)n_l$, and $(1 + \eta)^3(1 + \vartheta)^{-2} = (1 + \phi)^2$. Here, $P_{lg}^{\infty}$ and $P_{cg}^{\infty}$ are the equilibrium pressures on the gas-liquid and gas-crystal curves, respectively. As a rule, $|\eta|, |\vartheta| \ll 1$. Therefore, $|\phi| \ll 1$ as well. Relation (66) implies that inequality (65) holds at

$$P/P_{cg}^{\infty} > \zeta^{\frac{1+\phi}{3\vartheta}}.$$  \hspace{1cm} (67)

That is, at $T \to 0$ the rate of formation of liquid nuclei is much higher than that for crystal nuclei, if the gas is isothermally compressed at a pressure $P$ exceeding $P_{cg}^{\infty}$ by $\zeta^{\frac{1+\phi}{3\vartheta}}$ times. The quantity $\bar{\alpha}_{cg}$ can be estimated in the following way. By the rate of formation of crystal nuclei in a liquid, we can find $\bar{\alpha}_{cl}$: usually, $\bar{\alpha}_{cl} \approx (0.1 \div 0.2)\alpha_{gl}$ (for temperatures close to the melting one; see Table III.1 in [99]). It is natural to assume that $\bar{\alpha}_{cg} = \alpha_{gl} + \bar{c}\bar{\alpha}_{cl}$, where $\bar{c} \approx -1$, if the density of a crystal is less than that of a liquid, and $\bar{c} \approx 1$ in the opposite case. For most substances, the crystal is denser than the liquid ($\vartheta \approx 0.1$). Therefore, we expect for them that $\bar{\alpha}_{cg} \approx \alpha_{gl} + \bar{c}\bar{\alpha}_{cl}$, i.e., $\eta \approx 0.15$. However, for some substances (e.g., ice) $\eta$ and
ϑ are significantly different and can be negative. For the characteristic values η = 0.15 and ϑ = 0.1, we get φ ≈ 0.1, and (67) gives $P/P_{cg} > \zeta^{11}$. For the inert elements, the triple point corresponds to $P_3 \sim 1 \text{ atm}$. Therefore, at $T \ll T_3$ we have $P_{cg} \ll 1 \text{ atm}$. According to the analysis in Sect. 3, at $T \ll T_3$ the value of ζ is close to 1. Therefore, the pressure $P > \zeta^{11}P_{cg}$ at which the gas should condense into droplets is quite achievable.

It was asserted in some works [131, 137] that, for the vapor–crystal and vapor–liquid transitions, one needs to set $B = B'e^{Cq/(k_bT)}$ in formula (59). Here, the constant $C$ depends on the mechanism ($|C| \simeq 1$), $q$ is the latent heat of sublimation or evaporation, and $B'$ may slightly depend on $T$. Above, we neglected the factor $e^{Cq/(k_bT)}$. This is justified, if the phase transition occurs at a not too high supersaturation (in this case, the critical radius $r$ is large, and, therefore, $W \gg |C|q$).

For the surface mechanism of formation of nuclei, the formulae are significantly more complicated, especially for crystalline nuclei. In the last case, the work $W_c$ depends also on the relationship of the crystalline structures of a nucleus and the substrate [98, 130, 131, 133, 135, 137]. We did not make estimates for this case. Most likely, the ratio $P/P_{cg}$ is not too different from (67). Therefore, if the microstructures of the wall and crystal nuclei are strongly different and the wall is very smooth, we may expect that at the pressure $P > (2 \div 3)P_{cg}$ the surface formation of liquid nuclei is more probable, than the surface formation of crystal nuclei. In this case, the gas should condense into a liquid when compressed. Moreover, if atoms of a gas interact weakly with atoms of the walls, then the bulk formation of nuclei (drops or crystals) should be more intense, as compared with the formation of nuclei on the walls.

Our analysis is rather crude, but the main conclusions are apparently qualitatively right. Thus, the experiment on gas compression should be carried out with different walls of vessels at several different temperatures $T \ll T_3$. The condensation of a gas into a liquid has to be more probable than the crystallization, provided that (i) the microstructures of the wall and crystal nuclei are significantly different (or atoms of the gas interact weakly with atoms of the wall and relation (67) holds) and (ii) the gas is purified from impurities. Condition (i) can be fulfilled by covering the internal surfaces of the walls of a vessel with a solid amorphous substance [97, 98] or with a microlayer of helium-II. Perhaps, this is the simplest way to obtain the underliquid.

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