

## IX. IDEAL BOSE-EINSTEIN SYSTEMS

### IX.1. The phonon quantum field.

The classical mechanical model of a crystal lattice has been developed in §IV.4., where it has been shown that the expansion into normal modes of the displacements and momenta of a generic point-like atom in a lattice site can be definitely written in the form

$$Z_{\alpha, \mathbf{N}}(t) = \sum_{r, \mathbf{K}} \frac{Q_r(\mathbf{K})}{\sqrt{2N}} a_{\alpha r}(\mathbf{K}) \exp\{-i\omega_r(\mathbf{K})t + i\mathbf{K} \cdot \mathbf{N}\} + \text{c.c.} \quad (1.1a)$$

$$P_{\alpha, \mathbf{N}}(t) = \sum_{r, \mathbf{K}} m\omega_r(\mathbf{K}) \frac{Q_r(\mathbf{K})}{\sqrt{2N}} a_{\alpha r}(\mathbf{K}) \exp\{-i\omega_r(\mathbf{K})t + i\mathbf{K} \cdot \mathbf{N} - i\pi/2\} + \text{c.c.} \quad (1.1b)$$

in which we have set for short

$$\sum_{r, \mathbf{K}} := \sum_{r=1}^{3A} \sum_{\mathbf{K} \in \mathcal{B}}$$

and where the lattice index  $\mathbf{N} \equiv n_x \mathbf{a} + n_y \mathbf{b} + n_z \mathbf{c}$ , with  $\mathbf{a} = a\hat{\mathbf{i}}, \mathbf{b} = b\hat{\mathbf{j}}, \mathbf{c} = c\hat{\mathbf{k}}$  and  $(n_x, n_y, n_z) \in \mathbf{Z}^3$  labels the position of a cell, whereas the site indices  $\alpha, \beta, \dots$  run from 1 to  $3A$ . We recall that, under the assumption of *periodic boundary conditions* upon the faces of the crystal sample, which is supposed to be a parallelepiped for the sake of simplicity, one definitely finds that  $n_x = 1, \dots, N_x; n_y = 1, \dots, N_y; n_z = 1, \dots, N_z$ , where  $(N_x, N_y, N_z) \in \mathbf{N}^3$ , so that  $N := N_x N_y N_z$  is the total number of cells of the solid lattice. Accordingly, if we suppose *e.g.* the natural numbers  $N_x, N_y, N_z$  to be all even, then the lengths of the sides of the crystal sample are given by  $L_x = aN_x, L_y = bN_y, L_z = cN_z$ , whereas the wave vectors  $\mathbf{K}$  and the wave numbers  $\mathbf{k}$  of the so called *Brillouin's zone of*

the reciprocal lattice are respectively given by

$$K_x = 2\pi k_x / L_x, \quad k_x = \pm 1, \pm 2, \dots, \pm N_x / 2 \quad (1.2a)$$

$$K_y = 2\pi k_y / L_y, \quad k_y = \pm 1, \pm 2, \dots, \pm N_y / 2 \quad (1.2b)$$

$$K_z = 2\pi k_z / L_z, \quad k_z = \pm 1, \pm 2, \dots, \pm N_z / 2 \quad (1.2c)$$

in such a way that the total number of wave vectors of the Brillouin's zone keeps to be equal to  $N$  and the total number of degrees of freedom of the solid sample equal to  $3AN$ . The complex coefficients  $a_{\alpha r}(\mathbf{K}) = a_{\alpha r}^*(-\mathbf{K})$  are the entries of the unitary matrix  $[u(\mathbf{K})]_{\alpha r}$ , which is called the *polarization matrix* associated to a generic wave vector  $\mathbf{K}$  belonging to the Brillouin's zone. The polarization matrix diagonalizes the hermitean matrix  $\gamma_{\alpha\beta}(\mathbf{K})$  of eq. (4.21) in §IV.4. The complex coefficients  $Q_r(\mathbf{K})$  are just the *amplitudes of the normal modes* of the elastic vibrations of the crystal sample. Within the quadratic approximation, the hamiltonian of the crystal lattice can be expressed, in terms of the normal modes, as a sum of independent harmonic oscillations

$$H = \mathcal{V}_0 + \sum_{r, \mathbf{K}} m\omega_r^2(\mathbf{K}) Q_r^*(\mathbf{K}) Q_r(\mathbf{K}) \quad (1.3)$$

The equations of motion can be obtained in the hamiltonian form starting from the Poisson's brackets

$$\{Q_r(\mathbf{K}), Q_s^*(\mathbf{K}')\} = \frac{-i}{m\omega_r(\mathbf{K})} \delta_{rs} \delta_{\mathbf{K}\mathbf{K}'} \quad (1.4a)$$

$$\{Q_r(\mathbf{K}), Q_s(\mathbf{K}')\} = \{Q_r^*(\mathbf{K}), Q_s^*(\mathbf{K}')\} = 0 \quad (1.4b)$$

the solutions being

$$Q_r(\mathbf{K}, t) = Q_r(\mathbf{K}) \exp\{-i\omega_r(\mathbf{K})t\} \quad (1.5)$$

Now it is convenient to introduce the so called *standard holomorphic coordinates* according to the rule

$$A_r(\mathbf{K}) := Q_r(\mathbf{K}) \sqrt{m\omega_r(\mathbf{K})/\hbar}, \quad A_r^*(\mathbf{K}) := Q_r^*(\mathbf{K}) \sqrt{m\omega_r(\mathbf{K})/\hbar} \quad (1.6)$$

in such a way that the Poisson's brackets become

$$\{A_r(\mathbf{K}), A_s^*(\mathbf{K}')\} = -\frac{i}{\hbar} \delta_{rs} \delta_{\mathbf{K}\mathbf{K}'} \quad (1.7a)$$

$$\{A_r(\mathbf{K}), A_s(\mathbf{K}')\} = \{A_r^*(\mathbf{K}), A_s^*(\mathbf{K}')\} = 0 \quad (1.7b)$$

whilst the hamiltonian function takes the form

$$H = \mathcal{V}_0 + \sum_{r, \mathbf{K}} \hbar \omega_r(\mathbf{K}) A_r(\mathbf{K}) A_r^*(\mathbf{K}) \quad (1.8)$$

From the previous formulae it appears clear that, within the quadratic approximation and once the rigid space translations and rotations have been left aside, the dynamics of our crystal solid is equivalent to that one of an assembly of  $3AN$  independent linear harmonic oscillators. In particular, the transition to the quantum theory is accomplished by means of the *correspondence principle*, *i.e.* under the replacements of the holomorphic standard coordinates with the so called *annihilation and creation* operators, acting on a linear vector space of quantum states, and under the replacements of the Poisson's brackets (2.7) with the following *canonical commutation relations*: namely,

$$[\hat{A}_r(\mathbf{K}), \hat{A}_s^\dagger(\mathbf{K}')] = \delta_{rs} \delta_{\mathbf{K}\mathbf{K}'} \quad (1.9a)$$

$$[\hat{A}_r(\mathbf{K}), \hat{A}_s(\mathbf{K}')] = [\hat{A}_r^\dagger(\mathbf{K}), \hat{A}_s^\dagger(\mathbf{K}')] = 0 \quad (1.9b)$$

where  $\hat{A}_r(\mathbf{K})$  do represent linear operators acting upon the vector space of the quantum states of the crystal lattice, whereas  $\hat{A}_r^\dagger(\mathbf{K})$  denote their adjoints. In so doing, from eq. (1.8) and the correspondence principle, the hamiltonian self-adjoint operator can be expressed in the form

$$\hat{H} = U_0 + \sum_{r, \mathbf{K}} \hbar \omega_r(\mathbf{K}) \hat{A}_r^\dagger(\mathbf{K}) \hat{A}_r(\mathbf{K}) \quad (1.10)$$

where the so called zero-point energy turns out to be

$$U_0 := \mathcal{V}_0 + \sum_{r, \mathbf{K}} \hbar \omega_r(\mathbf{K}) / 2 .$$

It appears to be clear that the non-negative operators  $\hat{A}_r^\dagger(\mathbf{K})\hat{A}_r(\mathbf{K})$  do possess integer non-negative eigenvalues  $N_r(\mathbf{K}) = 0, 1, 2, \dots$  which are interpreted as the *numbers of phonons* of a given polarization  $r$ , a given tern of wave numbers  $\mathbf{K}$  and a given energy  $\hbar\omega_r(\mathbf{K})$ . The hamiltonian operator turns out to be positive definite and from the canonical commutation relations (1.9) we can readily derive the eigenvalues and the eigenstates of  $\hat{H}$ : namely,

$$E(\{N_r(\mathbf{K})\}) = U_0 + \sum_{r,\mathbf{K}} \hbar\omega_r(\mathbf{K}) N_r(\mathbf{K}), \quad N_r(\mathbf{K}) = 0, 1, 2, \dots \quad (1.11)$$

The number  $N = \sum_{r,\mathbf{K}} N_r(\mathbf{K})$  does indeed represent the total number of phonons which are present in the crystal lattice and turns out to be unbounded.

The setting up of the eigenstates leads to the well known construction of the so called Fock space of states [ Wladimir A. Fock (1932): Z. Physik **75**, 622 ] which can be done as follows. The ground state  $|0\rangle$  is called the *vacuum state* and is defined by

$$\hat{A}_r(\mathbf{K})|0\rangle \equiv 0 \equiv \langle 0|\hat{A}_r^\dagger(\mathbf{K}), \quad \forall r = 1, 2, \dots 3A, \forall \mathbf{K} \in \mathcal{B}. \quad (1.12)$$

It corresponds to the *absence of elastic excitations* in the solid sample and its energy is just the equilibrium energy  $U_0$ . Furthermore, we suppose it to be normalized, *i.e.*

$$\langle 0|0\rangle = 1. \quad (1.13)$$

Let us now construct the 1-phonon energy eigenstates: if we set

$$|r \mathbf{K}\rangle \equiv \hat{A}_r^\dagger(\mathbf{K})|0\rangle \quad (1.14)$$

we can immediately check that we have

$$\hat{H}|r \mathbf{K}\rangle = \hbar\omega_r(\mathbf{K})|r \mathbf{K}\rangle$$

so that  $|r \mathbf{K}\rangle$  does represent the state vector of one phonon of given polarization, wave number and energy. Moreover, the 1-phonon energy eigenstates do form a basis of the 1-phonon linear vector space  $\mathcal{V}_1$ , since we evidently have

$$\langle \mathbf{K}' s | r \mathbf{K} \rangle = \delta_{rs} \delta_{\mathbf{K}\mathbf{K}'} . \quad (1.15)$$

Notice that  $\dim \mathcal{V}_1 = 3AN$ . It is worth while to observe that, after quantization, the coordinates and momenta of the atoms of the crystal lattice do become operator valued expressions. Precisely, from eq.s (1.1) and (1.6) we get

$$\begin{aligned} \widehat{Z}_{\alpha, \mathbf{N}}(t) &= \sum_{r, \mathbf{K}} \sqrt{\hbar/2Nm\omega_r(\mathbf{K})} \times \\ &\times \widehat{A}_r(\mathbf{K}) a_{\alpha r}(\mathbf{K}) \exp\{-i\omega_r(\mathbf{K})t + i\mathbf{K} \cdot \mathbf{N}\} + \text{h.c.} \end{aligned} \quad (1.16a)$$

$$\begin{aligned} \widehat{P}_{\alpha, \mathbf{N}}(t) &= \sum_{r, \mathbf{K}} \sqrt{\hbar m\omega_r(\mathbf{K})/2N} \times \\ &\times \widehat{A}_r(\mathbf{K}) a_{\alpha r}(\mathbf{K}) \exp\{-i\omega_r(\mathbf{K})t + i\mathbf{K} \cdot \mathbf{N} - i\pi/2\} + \text{h.c.} \end{aligned} \quad (1.16b)$$

It follows therefrom that, taking eq. (4.8) of Chapter IV and eq.s (1.12) and (1.14) suitably into account, we can express the 1-phonon normalized wave functions in the lattice space coordinates by means of the matrix elements

$$\begin{aligned} \Psi_{\mathbf{K}}^r(\alpha, \mathbf{N}; t) &:= \langle 0 | \widehat{Z}_{\alpha, \mathbf{N}}(t) | r \mathbf{K} \rangle \sqrt{2m\omega_r(\mathbf{K})/\hbar} \\ &= a_{\alpha r}(\mathbf{K}) U_{\mathbf{K}}(\mathbf{N}) \exp\{-i\omega_r(\mathbf{K})t\} \\ &:= \langle \mathbf{N} \alpha | r \mathbf{K} \rangle_t . \end{aligned} \quad (1.17)$$

As a matter of fact we find

$$\begin{aligned} \langle 0 | \widehat{Z}_{\alpha, \mathbf{N}}(t) | r \mathbf{K} \rangle &= \sum_{s, \mathbf{K}'} \sqrt{\hbar/2Nm\omega_s(\mathbf{K}')} \times \\ &\times \left\{ \langle 0 | \widehat{A}_s(\mathbf{K}') | r \mathbf{K} \rangle a_{\alpha s}(\mathbf{K}') \exp[-i\omega_s(\mathbf{K}')t + i\mathbf{K}' \cdot \mathbf{N}] \right. \\ &+ \left. \langle 0 | \widehat{A}_s^\dagger(\mathbf{K}') | r \mathbf{K} \rangle a_{\alpha s}^*(\mathbf{K}') \exp[i\omega_s(\mathbf{K}')t - i\mathbf{K}' \cdot \mathbf{N}] \right\} \\ &= a_{\alpha r}(\mathbf{K}) \exp\{-i\omega_r(\mathbf{K})t + i\mathbf{K} \cdot \mathbf{N}\} \sqrt{\hbar/2Nm\omega_r(\mathbf{K})} \\ &= a_{\alpha r}(\mathbf{K}) U_{\mathbf{K}}(\mathbf{N}) \exp\{-i\omega_r(\mathbf{K})t\} \sqrt{\hbar/2m\omega_r(\mathbf{K})} , \end{aligned} \quad (1.18)$$

whence eq. (1.17) immediately follows. To conclude our analysis of the 1-phonon quantum states, we write down the generic normalized element of  $\mathcal{V}_1$ : namely,

$$|\varphi_1\rangle := \sum_{r,\mathbf{K}} C_r(\mathbf{K}) \widehat{A}_r^\dagger(\mathbf{K})|0\rangle \in \mathcal{V}_1 \quad (1.19)$$

where the complex coefficients  $\{C_r(\mathbf{K}); r = 1, \dots, 3A, \mathbf{K} \in \mathcal{B}\}$  do fulfill

$$\sum_{r,\mathbf{K}} |C_r(\mathbf{K})|^2 = 1. \quad (1.20)$$

The corresponding wave function in the lattice space coordinates

$$\varphi_1(\alpha, \mathbf{N}; t) = \sum_{r,\mathbf{K}} C_r(\mathbf{K}) \Psi_{\mathbf{K}}^r(\alpha, \mathbf{N}; t) \quad (1.21)$$

does actually represent the propagation inside the solid sample of one phonon without any definite polarization, wave numbers and energy.

Let us now continue by building up the 2-phonon energy eigenstates. To this concern, we have to distinguish two cases. As a first possibility we consider the normalized state

$$|r\mathbf{K}\rangle_2 := \left[ \widehat{A}_r^\dagger(\mathbf{K}) \right]^2 |0\rangle / \sqrt{2!} \quad (1.22)$$

which describes two identical phonons with the very same polarization and wave numbers.

As a second possibility, we consider the normalized state

$$|r_1\mathbf{K}_1 r_2\mathbf{K}_2\rangle_2 := \widehat{A}_{r_1}^\dagger(\mathbf{K}_1) \widehat{A}_{r_2}^\dagger(\mathbf{K}_2)|0\rangle \quad (1.23)$$

which describes two different phonons with either different polarizations  $r_1 \neq r_2$  or different wave numbers  $\mathbf{K}_1 \neq \mathbf{K}_2$ , or even different polarizations and wave numbers  $r_1 \neq r_2, \mathbf{K}_1 \neq \mathbf{K}_2$ . It is important to remark that in both the above cases, owing to the canonical commutation relations (1.9b), the 2-phonon states turn out to be manifestly

symmetrical with respect to the phonons exchange. It is also straightforward to check that the states (1.22) and (1.23) are indeed eigenstates of the hamiltonian operator: namely,

$$\widehat{H} |r \mathbf{K}\rangle_2 = U_0 + 2\omega_r(\mathbf{K}) |r \mathbf{K}\rangle_2 \quad (1.24a)$$

$$\widehat{H} |r_1 \mathbf{K}_1 r_2 \mathbf{K}_2\rangle_2 = U_0 + \{\omega_{r_1}(\mathbf{K}_1) + \omega_{r_2}(\mathbf{K}_2)\} |r_1 \mathbf{K}_1 r_2 \mathbf{K}_2\rangle_2 \quad (1.24b)$$

To sum up, if we set

$$|r_1 \mathbf{K}_1 r_2 \mathbf{K}_2\rangle := \begin{cases} (1/\sqrt{2!})[\widehat{A}_r^\dagger(\mathbf{K})]^2|0\rangle, & \text{if } r_1 = r_2 \text{ and } \mathbf{K}_1 = \mathbf{K}_2; \\ \widehat{A}_{r_1}^\dagger(\mathbf{K}_1)\widehat{A}_{r_2}^\dagger(\mathbf{K}_2)|0\rangle, & \text{otherwise,} \end{cases} \quad (1.25)$$

we obtain an orthonormal basis of the 2-phonon energy eigenstates in the completely symmetric space  $\mathcal{V}_2^{(+)} \equiv S\{\mathcal{V}_1 \otimes \mathcal{V}_1\}$ , *i.e.* the symmetric tensor product of two 1-phonon linear vector spaces. As a matter of fact, one can readily check that we have

$$\langle \mathbf{K}'_2 s_2 \mathbf{K}'_1 s_1 | r_1 \mathbf{K}_1 r_2 \mathbf{K}_2 \rangle = \delta_{r_1 s_1} \delta_{\mathbf{K}_1 \mathbf{K}'_1} \delta_{r_2 s_2} \delta_{\mathbf{K}_2 \mathbf{K}'_2} \quad (1.26)$$

In analogy with the 1-phonon case, we can readily set up the generic 2-phonon normalized quantum state

$$|\varphi_2\rangle := \sum_{r_1, \mathbf{K}_1} \sum_{r_2, \mathbf{K}_2} C(r_1, \mathbf{K}_1; r_2, \mathbf{K}_2) |r_1 \mathbf{K}_1 r_2 \mathbf{K}_2\rangle \quad (1.27)$$

where the symmetric complex coefficients  $C(r_1, \mathbf{K}_1; r_2, \mathbf{K}_2)$  fulfill

$$\sum_{r_1, \mathbf{K}_1} \sum_{r_2, \mathbf{K}_2} |C(r_1, \mathbf{K}_1; r_2, \mathbf{K}_2)|^2 = 1. \quad (1.28)$$

Finally, in order to describe  $N$ -phonon states, let us consider a set of phonon numbers  $\{N_r(\mathbf{K}) = 0, 1, 2, \dots \mid r = 1, 2, \dots, 3A, \mathbf{K} \in \mathcal{B}\}$  such that  $\sum_{r, \mathbf{K}} N_r(\mathbf{K}) = N$ . Then the generic  $N$ -phonon normalized energy eigenstate can be written as

$$|\{N_r(\mathbf{K})\}\rangle_N := \prod_{r, \mathbf{K}} [N_r(\mathbf{K})!]^{-1/2} [A_r^\dagger(\mathbf{K})]^{N_r(\mathbf{K})}|0\rangle \quad (1.30)$$

which satisfies – see eq. (1.11)

$$\widehat{H} |\{N_r(\mathbf{K})\}\rangle_N = E_N(\{N_r(\mathbf{K})\}) |\{N_r(\mathbf{K})\}\rangle_N \quad (1.31)$$

$${}_M \langle \mathbf{K}' s | r \mathbf{K} \rangle_N = \delta_{MN} \delta_{r_1 s_1} \delta_{\mathbf{K}_1 \mathbf{K}'_1} \delta_{r_2 s_2} \delta_{\mathbf{K}_2 \mathbf{K}'_2} \cdots \delta_{r_N s_N} \delta_{\mathbf{K}_N \mathbf{K}'_N} \quad (1.32)$$

It is very important to remark once again that, owing to the canonical commutation relations (1.9), the eigenstates (1.30) of the crystal lattice hamiltonian are completely symmetric with respect to the exchanges of any pair of polarization and wave numbers labels. As a consequence, a given set of phonon numbers  $\{N_r(\mathbf{K})\}$  *uniquely* specifies, up to a phase, one particular  $N$ -phonon eigenstate of  $\widehat{H}$  and, thereby, phonons do obey the *Bose–Einstein statistics*, *i.e.* phonons are bosons.

The  $N$ -phonon energy eigenfunctions in the lattice space coordinates representation can be readily obtained by generalizing eq. (1.17): namely,

$$\begin{aligned} \Psi_N(\{N_r(\mathbf{K})\}; t) &= \frac{1}{\sqrt{N!}} \sum_{[\text{Perm}]} \{ \Psi_{\mathbf{K}_1}^{r_1}(P_1; t) \Psi_{\mathbf{K}_2}^{r_2}(P_2; t) \cdots \Psi_{\mathbf{K}_N}^{r_N}(P_N; t) \} \\ &:= \langle \mathbf{N}_N \alpha_N \cdots \mathbf{N}_2 \alpha_2 \mathbf{N}_1 \alpha_1 | r_1 \mathbf{K}_1 r_2 \mathbf{K}_2 \cdots r_N \mathbf{K}_N \rangle_t \end{aligned} \quad (1.33)$$

where  $[\text{Perm}]$  denotes the generic permutation  $(1, 2, \dots, N) \mapsto (P_1, P_2, \dots, P_N)$  of the  $N$  pairs of lattice coordinates  $(\alpha_1 \mathbf{N}_1 \alpha_2 \mathbf{N}_2 \cdots \alpha_N \mathbf{N}_N)$  – see eq. (5.2) of Chapter VI. Actually, if some of the phonon numbers  $N_r(\mathbf{K})$  are bigger than one, then some of the polarization and wave number pairs do coincide and we can eventually write the orthonormality and completeness relationships of the  $N$ -phonon energy eigenfunctions basis in the lattice space coordinates representation: respectively,

$$\begin{aligned} \sum_{\alpha_1, \mathbf{N}_1} \cdots \sum_{\alpha_N, \mathbf{N}_N} \Psi_N(\{N_r(\mathbf{K})\}; t) \Psi_N^*(\{N_s(\mathbf{K}')\}; t) &= \delta_{r_1 s_1} \delta_{\mathbf{K}_1 \mathbf{K}'_1} \cdots \delta_{r_N s_N} \delta_{\mathbf{K}_N \mathbf{K}'_N} \\ \sum_{r_1, \mathbf{K}_1} \cdots \sum_{r_N, \mathbf{K}_N} \Psi_N(\{N_r(\mathbf{K})\}; t) \Psi_N^*(\{N_s(\mathbf{K}')\}; t) &= \delta_{\alpha_1 \beta_1} \delta_{\mathbf{N}_1 \mathbf{N}'_1} \cdots \delta_{\alpha_N \beta_N} \delta_{\mathbf{N}_N \mathbf{N}'_N} \end{aligned}$$

Finally, we can write the generic normalized element of the  $N$ -phonon completely symmetric linear vector space (the completely symmetric product of  $N$  1-phonon vector



spaces  $\mathcal{V}_1$ )

$$\mathcal{V}_N^{(+)} := S\{\underbrace{\mathcal{V}_1 \otimes \mathcal{V}_1 \otimes \dots \otimes \mathcal{V}_1}_{N \text{ times}}\}$$

in the form

$$|\varphi_N\rangle := \sum_{r_1, \mathbf{K}_1} \sum_{r_2, \mathbf{K}_2} \dots \sum_{r_N, \mathbf{K}_N} C(r_1, \mathbf{K}_1; r_2, \mathbf{K}_2; \dots; r_N, \mathbf{K}_N) |\{N_r(\mathbf{K})\}\rangle_N \quad (1.34)$$

with

$$\sum_{r_1, \mathbf{K}_1} \sum_{r_2, \mathbf{K}_2} \dots \sum_{r_N, \mathbf{K}_N} |C(r_1, \mathbf{K}_1; r_2, \mathbf{K}_2; \dots; r_N, \mathbf{K}_N)|^2 = 1 \quad (1.35)$$

the lattice space coordinates representation being

$$\begin{aligned} \langle \mathbf{N}_N \alpha_N \dots \mathbf{N}_2 \alpha_2 \mathbf{N}_1 \alpha_1 | \varphi_N \rangle_t = \\ \sum_{r_1, \mathbf{K}_1} \sum_{r_2, \mathbf{K}_2} \dots \sum_{r_N, \mathbf{K}_N} C(r_1, \mathbf{K}_1; r_2, \mathbf{K}_2; \dots; r_N, \mathbf{K}_N) \Psi_N(\{N_r(\mathbf{K})\}; t) . \end{aligned} \quad (1.36)$$

To end up, we are now able to write the generic normalized element of the Fock space of the phonon states, which is infinite dimensional,

$$\mathcal{F}_{\text{phonons}} \equiv \mathbf{C} \oplus \mathcal{V}_1 \oplus \mathcal{V}_2^{(+)} \oplus \dots \oplus \mathcal{V}_N^{(+)} \dots$$

in the form

$$|\Phi\rangle_t = \sum_{N=0}^{\infty} C_N |\varphi_N\rangle_t , \quad \sum_{N=0}^{\infty} |C_N|^2 = 1$$

which summarizes our explicit construction of the phonon states propagating inside a crystal solid sample, the structure of which is characterized by the canonical quantum algebra (1.9) and the hamiltonian operator (1.10).

## IX.2. Thermal equilibrium of a solid crystal.

It appears to be clear that, from the classical expression (1.3) of the hamiltonian function and from the corresponding expression (1.11) for the eigenvalues of the quantum hamiltonian operator (1.10), the energy of a solid sample may be considered as arising from an assembly of  $3AN$  *non-interacting* one dimensional harmonic oscillators, of which the characteristic frequencies  $\omega_r(\mathbf{K})$  are determined by the nature of the microscopic atomic interactions within the crystal lattice.

Classically, each one of the  $3AN$  normal modes of vibrations does correspond to a wave of *distortion* of the lattice sites propagating inside the solid sample, *i.e.* elastic waves, the maximal frequencies of which are typically ranging from  $10^{13} \div 10^{15}$  Hz. The canonical quantization of those normal modes of vibration gives rise to the concept of phonons, *i.e.* non-interacting quanta or *quasi-particles* propagating inside the crystal solid, the typical characteristic frequencies of propagation being within the sound interval  $\nu_s = 16 \div 1.8 \times 10^5$  Hz. Actually, we can say that the quantum mechanical treatment of the normal modes of vibrations of a crystal lattice just leads to the picture of an *ideal gas of free phonons* enclosed within the solid sample.

The statistical thermodynamics of the solid can be better formulated in terms of the canonical ensemble, as it has been done at the end of §IV.4. – see the classical canonical partition function (4.43). The quantization of the non-interacting elastic distortion waves of the crystal lattice leads immediately to the canonical quantum partition function

$$\begin{aligned}
 Z_{3AN}(T, V) &= \text{Tr} \exp\{-\widehat{H}/kT\} \\
 &= \exp\{-U_0/kT\} \prod_{r, \mathbf{K}} \sum_{N_r(\mathbf{K})=0}^{\infty} \exp\{-N_r(\mathbf{K})\hbar\omega_r(\mathbf{K})/kT\} \\
 &= \exp\{-U_0/kT\} \prod_{r, \mathbf{K}} (1 - \exp\{-\hbar\omega_r(\mathbf{K})/kT\})^{-1}
 \end{aligned} \tag{2.1}$$

whence the Helmholtz free energy readily follows

$$F_{3AN}(T, V) = U_0 + kT \sum_{r, \mathbf{K}} \ln(1 - \exp\{-\hbar\omega_r(\mathbf{K})/kT\}) \quad (2.2)$$

together with the internal energy

$$U_{3AN}(T, V) = U_0 + \sum_{r, \mathbf{K}} \frac{\hbar\omega_r(\mathbf{K})}{\exp\{\hbar\omega_r(\mathbf{K})/kT\} - 1} \quad (2.3)$$

and the fixed volume heat capacity

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = k \sum_{r, \mathbf{K}} \frac{[\hbar\omega_r(\mathbf{K})/kT]^2 \exp\{\hbar\omega_r(\mathbf{K})/kT\}}{[\exp\{\hbar\omega_r(\mathbf{K})/kT\} - 1]^2}. \quad (2.4)$$

It is worth while to remark that, according to eq.s (1.2), the modulus of the lowest non-vanishing wave number is  $2\pi/\sqrt{L_x^2 + L_y^2 + L_z^2}$  so that, if we denote by  $\bar{v}$  the average sound velocity in the crystal sample, we can say that the minimal attainable angular frequency of the elastic waves propagating inside the solid is of the order  $\omega_{\min} \simeq 2\pi\bar{v}/\sqrt{L_x^2 + L_y^2 + L_z^2}$ . This means that, for low temperatures such that  $kT < \hbar\omega_{\min}$ , there is not enough thermal energy to excite even one single phonon. As a consequence, the solid sample will certainly lie in the vacuum state and its entropy is zero according to the Nerst's theorem.

To proceed further, we must have a knowledge of the frequency spectrum of the solid. To achieve this knowledge from first principles is a very hard task of condensed matter physics. Accordingly, either one obtains that spectrum from experiments, which is highly non-trivial too, or else one makes certain plausible assumptions about it. Historically, the first realistic theory of a solid crystal has been proposed by Albert Einstein (1907) *Jb. Radioakt.* **4**, 411. The Einstein's assumption was that all the characteristic frequencies of a solid are equal: namely,  $\omega_r(\mathbf{K}) = \omega_E$ ,  $\forall r = 1, 2, \dots, 3A$ ,  $\forall \mathbf{K} \in \mathcal{B}$ . Consequently, we immediately recover from (2.4) the Einstein's formula for the heat capacity

$$C_V^{(\text{Einstein})} = 3ANk \frac{x^2 e^x}{(e^x - 1)^2} \quad [x := \beta\hbar\omega_E] \quad (2.5)$$

For  $kT \gg \omega_E$  the Einstein's result nicely tends towards the classical Dulong–Petit law. At sufficiently low temperatures, for large  $x \gg 1$ , the Einstein's expression of the heat capacity falls off exponentially to zero, at a too fast rate in comparison with experimental data. Nevertheless, the breakthrough which the Einstein's approach did provide was the main idea that quantum mechanics is the key ingredient to understand the observed departure of the heat capacity of a solid from the classical equipartition theorem.

The reason why the Einstein's theory of solids is not completely satisfactory stays upon its oversimplification of the characteristic frequencies spectrum. This basic difficulty has been overcome in the Debye's theory of solids (1912) [ Peter Joseph William Debye (Maastricht 24.3.1884 – Ithaca 2.11.1966) ] whose main assumptions will be discussed here below [ see in particular Bruno Touschek & Giancarlo Rossi (1970): *Meccanica statistica*, Boringhieri, Torino, pp. 170–186 ].

- (i) The main assumption in the Debye's theory is that the thermal excitation of a crystal lattice gives rise to collective motions of all the atoms, which manifest themselves in the form of *elastic waves*, typically *sound waves*. Of course, we have three modes of propagation: two transversal, corresponding to *torsion waves*, which propagate at a speed  $v_T$  and one longitudinal, corresponding to *contraction–dilatation waves*, which propagates at a speed  $v_L$ .
- (ii) In a first approximation one can disregard the *dispersion phenomena* and suppose that the speeds  $v_T$  and  $v_L$  do not depend upon frequencies. The elastic waves just correspond to the normal modes of vibration of the crystal lattice.
- (iii) Since the gap between the components of two nearest neighbour wave number vectors in the Brillouin zone  $\mathcal{B}$  is of the order  $2\pi/L$ , where  $L$  denotes the average linear size of the solid sample – see eq. (1.2) – it turns out that this gap is very small in units of the

inverse lattice spacing, so that we can safely perform the transition to the *continuum limit*. Each elastic wave is thereof characterized by its wave number vector  $\mathbf{K} \in \mathbf{R}^3$  such that  $|\mathbf{K}| \leq 2\pi/\sqrt{a^2 + b^2 + c^2} := K_{\max}$ , together with its polarization unit vector  $\hat{\mathbf{e}}_{\mathbf{K}}$  such that  $\mathbf{K} \cdot \hat{\mathbf{e}}_{\mathbf{K}} = 0$  for the transversal modes, whereas  $\mathbf{K} \cdot \hat{\mathbf{e}}_{\mathbf{K}} = K$  for the longitudinal mode. If dispersion phenomena are neglected, the angular frequency of each normal mode will be proportional to the wave number and the phase velocity will coincide with the group velocity: namely,

$$\omega_T(\mathbf{K}) = v_T|\mathbf{K}|, \quad \omega_L(\mathbf{K}) = v_L|\mathbf{K}|. \quad (2.6)$$

As a final assumption, we shall suppose that  $\omega_T(K_{\max}) \simeq \omega_L(K_{\max}) := \omega_D$ . For instance, if we consider a Cu crystal, we find a density  $\rho = 8.93 \text{ g cm}^{-3}$ , the elastic constant  $E = 1.2 \times 10^{12} \text{ g cm}^{-1} \text{ s}^{-2}$  and the torsion constant  $G = 0.4 \times 10^{12} \text{ g cm}^{-1} \text{ s}^{-2}$ , so that we obtain  $v_L = \sqrt{E/\rho} = 370 \text{ m s}^{-1}$  and  $v_T = \sqrt{G/\rho} = 220 \text{ m s}^{-1}$ .

Taking all the above assumptions suitably into account, we can express the total number of elastic normal modes, *i.e.* the total number of vibrational degrees of freedom, as

$$\begin{aligned} 3AN &= \sum_{r, \mathbf{K}} \approx \frac{3V}{(2\pi)^3} \int_0^{K_{\max}} 4\pi K^2 dK \\ &= \frac{V}{2\pi^2} \left( \frac{2}{v_T^3} + \frac{1}{v_L^3} \right) \int_0^{\omega_D} d\omega \omega^2 \\ &= \frac{V}{6\pi^2} \left( \frac{2}{v_T^3} + \frac{1}{v_L^3} \right) \omega_D^3. \end{aligned} \quad (2.7)$$

This means that the frequency spectrum of the elastic normal modes is supposed to be approximately continuous and the *density of the elastic normal modes* of a crystal solid, *i.e.* the number of elastic normal modes with frequencies between  $\omega$  and  $\omega + d\omega$  per unit of frequency  $d\omega$ , can be written as

$$\varrho_D(\omega) \approx \frac{V}{2\pi^2} \left( \frac{2}{v_T^3} + \frac{1}{v_L^3} \right) \omega^2 \vartheta(\omega_D - \omega). \quad (2.8)$$

It follows therefrom that, within the Debye's approximation, we can indeed recast the thermodynamic potentials in the form

$$F_{3AN}(T, V) \approx U_0 + kT \int_0^\infty d\omega \varrho_D(\omega) \ln(1 - \exp\{-\hbar\omega/kT\}) , \quad (2.9)$$

$$U_{3AN}(T, V) \approx U_0 + \int_0^\infty d\omega \varrho_D(\omega) \hbar\omega (\exp\{\hbar\omega/kT\} - 1)^{-1} , \quad (2.10)$$

$$C_V \approx k \int_0^\infty d\omega \varrho_D(\omega) (\hbar\omega/kT)^2 \exp\{\hbar\omega/kT\} (\exp\{\hbar\omega/kT\} - 1)^{-2} . \quad (2.11)$$

In the limit of very high temperatures, such that  $kT \gg \hbar\omega_D$ , we immediately obtain the leading behaviour

$$U_{3AN}(T, V) \stackrel{\beta\hbar\omega_D \ll 1}{\sim} U_0 + \int_0^\infty d\omega \varrho_D(\omega) = U_0 + 3ANkT \quad (2.12)$$

$$C_V \stackrel{\beta\hbar\omega_D \ll 1}{\sim} 3ANk \quad (2.13)$$

which is nothing but the Dulong–Petit law and does not depend upon the specific form of the spectral density. In the opposite limit of very low temperatures, the high frequencies become irrelevant – the main contributions to the integrals being from a neighbourhood of  $\omega = 0$  – so that the assumption of the absence of dispersion in the propagation of the elastic waves is quite realistic and experimentally fulfilled. In other words, the true spectral density of the normal modes and the Debye's expression (2.8) do indeed coincide when  $\omega \downarrow 0$ . By inserting eq. (2.8) in to eq. (2.10) and changing the integration variable according to  $x = \hbar\omega/kT$  we eventually obtain

$$U_{3AN}(T, V) \approx U_0 + 9ANkT \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^3 dx}{e^x - 1} \quad (2.14)$$

where we have introduced the so called *Debye's temperature*  $\Theta_D := (\hbar/k)\omega_D$ . In the very same way, after an integration by parts, we can obtain the following approximate expression for the heat capacity: namely,

$$C_V \approx 3NAk\mathcal{D}(T/\Theta_D) , \quad (2.15)$$

where the universal function

$$\mathcal{D}(\xi) := 12\xi^3 \int_0^{1/\xi} \frac{x^3 dx}{e^x - 1} - \frac{3/\xi}{e^{1/\xi} - 1} \quad (2.16)$$

is called the *Debye's function* and does not depend upon the specific kind of the crystal solid under consideration. We have the following leading behaviour:

(i) high temperature limit  $T \gg \Theta_D$

$$\lim_{\xi \rightarrow \infty} \mathcal{D}(\xi) = 1 ; \quad (2.17)$$

(ii) low temperature limit  $T \ll \Theta_D$

$$\mathcal{D}(\xi) \stackrel{\xi \downarrow 0}{\sim} 12\xi^3 \int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{4}{5} \pi^4 \xi^3 \quad (2.18)$$

so that we eventually find

$$C_V \stackrel{T \ll \Theta_D}{\sim} \frac{12\pi^4}{5\Theta_D^3} N A k T^3 = 464.4 \left( \frac{T}{\Theta_D} \right)^3 \text{ cal mol}^{-1} \text{ }^\circ\text{K}^{-1} . \quad (2.19)$$

Finally, from the approximate Helmholtz free energy (2.9) we can easily obtain the lattice entropy in the Debye's theory that reads

$$S_{3AN}(T, V) \approx 3ANk \left\{ 4 \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^3 dx}{e^x - 1} - \ln(1 - \exp[-\Theta_D/T]) \right\} \quad (2.20)$$

$$\stackrel{T \ll \Theta_D}{\sim} \frac{4\pi^4}{5\Theta_D^3} N A k T^3 = 154.8 \left( \frac{T}{\Theta_D} \right)^3 \text{ cal mol}^{-1} \text{ }^\circ\text{K}^{-1}$$

which correctly vanishes like  $T^3$  at low temperatures in agreement with the Nerst's theorem. It is clear from eq. (2.19) that a measurement of the low-temperature heat capacity of a solid does enable us not only to check the validity of the cubic law (2.19) but also to obtain an empirical value of the Debye's temperature  $\Theta_D$ . The value  $\Theta_D$  can also be obtained by computing the cut-off frequency  $\omega_D$  from a knowledge of the parameters  $AN/V, v_T, v_L,$

according to eq. (2.7). The closeness of these estimates is another strong evidence in support of the Debye's theory. As a matter of fact we find the following values in °K of  $\Theta_D$  from the specific heat measurements: namely,

Pb(88)    Ag(215)    Zn(308)    Cu(345)    Al(398)    NaCl(308)

and the corresponding values of  $\Theta_D$  from elastic constant measurements

Pb(73)    Ag(214)    Zn(305)    Cu(332)    Al(402)    NaCl(320)

whence we can conclude that the agreement is very good, taking the simplicity of the model into account.



## Appendix E: frequency spectrum $\nu$

### Elastic waves

infra-sound :  $0 \div 16$  Hz ;

sound :  $16 \div 1.8 \times 10^5$  Hz ;

ultra-sound :  $1.8 \times 10^5 \div 10^9$  Hz ;

hyper-sound :  $10^9 \div 10^{11}$  Hz ;

### Electromagnetic waves

long-waves :  $0 \div 10^4$  Hz ;

radio/TV-waves :  $10^4 \div 10^9$  Hz ;

IR-waves :  $10^9 \div 4 \times 10^{14}$  Hz ;

light-waves :  $4 \times 10^{14} \div 7 \times 10^{14}$  Hz ;

UV-waves :  $7 \times 10^{14} \div 10^{17}$  Hz ;

X-Rays :  $10^{17} \div 10^{21}$  Hz ;

$\gamma$ -Rays :  $10^{21} \div 10^{24}$  Hz .

Conversion factor :  $k/\hbar = 1.3 \times 10^{11}$  Hz/ $^{\circ}$ K .

Debye's angular frequencies from specific heat measurements :

$\omega_D(\text{Pb}) = 7.15 \times 10^{13}$  Hz  $\div$   $\omega_D(\text{C}) = 1.50 \times 10^{15}$  Hz .

Debye's angular frequencies from the elastic constants :

$\omega_D(\text{Pb}) = 5.93 \times 10^{13}$  Hz  $\div$   $\omega_D(\text{C}) = 1.48 \times 10^{15}$  Hz .

### IX.3. Thermal equilibrium of the radiation quantum field.

The classical mechanical treatment of the Maxwell's radiation field has been developed in §IV.5., where the radiation field is supposed to be contained within a cubic box of side  $L$ , with periodic boundary conditions on the walls. In such a situation and after choosing the Coulomb's or radiation's gauge  $\nabla \cdot \mathbf{A} = 0$ ,  $\varphi = 0$ , the components of the vector potential can be expanded as Fourier series as in eq. (IV.5.39): namely,

$$\mathbf{A}(t, \mathbf{r}) = \sum_{\mathbf{n}, \lambda} \mathbf{e}_\lambda(\mathbf{n}) q_\lambda(\mathbf{n}) \exp \left\{ -i\omega_{\mathbf{n}} t + \frac{2\pi i}{L} \mathbf{n} \cdot \mathbf{r} \right\} + \text{c.c.} , \quad (3.1)$$

where we have set

$$\sum_{\mathbf{n}, \lambda} := \sum_{n_x=-\infty}^{+\infty} \sum_{n_y=-\infty}^{+\infty} \sum_{n_z=-\infty}^{+\infty} \sum_{\lambda=1,2}$$

We definitely see that the radiation field in a box is dynamically equivalent to an infinite collection of linear harmonic oscillators with frequencies  $\nu(\mathbf{n}) = c|\mathbf{n}|/L$  and two possible polarizations for each frequency.

The amplitudes of the normal modes  $q_\lambda(\mathbf{n})$ ,  $q_\lambda^*(\mathbf{n})$  are the *holomorphic coordinates* of the radiation field and do satisfy the following Poisson's brackets

$$\{q_\lambda(\mathbf{n}), q_\sigma^*(\mathbf{m})\} = (2\pi c^2 / i\omega_{\mathbf{n}} L^3) \delta_{\lambda\sigma} \delta_{\mathbf{m}\mathbf{n}} , \quad (3.2a)$$

$$\{q_\lambda(\mathbf{n}), q_\sigma(\mathbf{m})\} = \{q_\lambda^*(\mathbf{n}), q_\sigma^*(\mathbf{m})\} = 0 . \quad (3.2b)$$

Furthermore, the Hamilton's function of the radiation field mechanical system, which turns out to be a conserved time independent quantity, can be expressed in a very simple way in terms of the holomorphic coordinates: actually,

$$W_{\text{rad}} \equiv H_{\text{rad}} = \frac{L^3}{2\pi c^2} \sum_{\mathbf{n}, \lambda} \omega_{\mathbf{n}}^2 q_\lambda(\mathbf{n}) q_\lambda^*(\mathbf{n}) . \quad (3.3)$$

It is very easy to check that the time evolution of the holomorphic coordinates is just provided by a phase factor, *viz.*

$$\begin{aligned} q_\lambda(\mathbf{n}, t) &= q_\lambda(\mathbf{n}) \exp \{-i\omega_\mathbf{n}t\} , \\ q_\lambda^*(\mathbf{n}, t) &= q_\lambda^*(\mathbf{n}) \exp \{+i\omega_\mathbf{n}t\} . \end{aligned} \quad (3.4)$$

*Rebus sic stantibus*, it appears to be clear that the quantization of the radiation field will closely follow, *mutatis mutandis*, the whole procedure already employed in the case of the crystal solid. First of all it is convenient to introduce the so called *standard holomorphic coordinates* for the radiation field according to the rule

$$a_\lambda(\mathbf{n}) := q_\lambda(\mathbf{n})\sqrt{L^3\omega_\mathbf{n}/2\pi\hbar c^2} , \quad a_\lambda^*(\mathbf{n}) := q_\lambda^*(\mathbf{n})\sqrt{L^3\omega_\mathbf{n}/2\pi\hbar c^2} \quad (3.5)$$

in such a way that the Poisson's brackets become

$$\{a_\lambda(\mathbf{n}), a_\sigma^*(\mathbf{n}')\} = -\frac{i}{\hbar} \delta_{\lambda\sigma} \delta_{\mathbf{nn}'} \quad (3.6a)$$

$$\{a_\lambda(\mathbf{n}), a_\sigma(\mathbf{n}')\} = \{a_\lambda^*(\mathbf{n}), a_\sigma^*(\mathbf{n}')\} = 0 \quad (3.6b)$$

whilst the hamiltonian function takes the form

$$H_{\text{rad}} = \sum_{\lambda, \mathbf{n}} \hbar\omega_\mathbf{n} a_\lambda(\mathbf{n})a_\lambda^*(\mathbf{n}) \quad (3.7)$$

The transition to the quantum theory is accomplished once again by means of the *correspondence principle*, *i.e.* under the replacements of the classical holomorphic standard coordinates with the so called *annihilation and creation* quantum operators, acting on a linear vector space of quantum states, and under the replacements of the Poisson's brackets (3.6) with the following *canonical commutation relations*: namely,

$$[\hat{a}_\lambda(\mathbf{n}), \hat{a}_\sigma^\dagger(\mathbf{n}')] = \delta_{\lambda\sigma} \delta_{\mathbf{nn}'} \quad (3.8a)$$

$$[\hat{a}_\lambda(\mathbf{n}), \hat{a}_\sigma(\mathbf{n}')] = [\hat{a}_\lambda^\dagger(\mathbf{n}), \hat{a}_\sigma^\dagger(\mathbf{n}')] = 0 \quad (3.8b)$$

where  $\hat{a}_\lambda(\mathbf{n})$  do represent linear operators acting upon the vector space of the quantum states of the radiation field, whereas  $\hat{a}_\lambda^\dagger(\mathbf{n})$  denote their adjoints. In so doing, from eq. (3.1) and the correspondence principle, the vector potential becomes an operator valued tempered distribution

$$\hat{\mathbf{A}}(x) = \sqrt{\frac{\hbar c}{L^3}} \sum_{\lambda, \mathbf{n}} k_0^{-1/2} \left\{ \mathbf{e}_\lambda(\mathbf{n}) \hat{a}_\lambda(\mathbf{n}) e^{-ik \cdot x} + \mathbf{e}_\lambda^*(\mathbf{n}) \hat{a}_\lambda^\dagger(\mathbf{n}) e^{ik \cdot x} \right\} \quad (3.9)$$

where we have employed the four-vector notation

$$x^\mu = (ct, \mathbf{r}) := x, \quad k^\mu = (k^0, \mathbf{k}) := k, \quad k^0 = \omega_{\mathbf{n}}/c, \quad \mathbf{k}_{\mathbf{n}} = 2\pi\mathbf{n}/L,$$

$$k \cdot x := k_\mu x^\mu = \omega_{\mathbf{n}}t - \mathbf{k}_{\mathbf{n}} \cdot \mathbf{r}.$$

From eq. (3.7) the energy and momentum self-adjoint operators are given by

$$\hat{H}_{\text{rad}} = \sum_{\lambda, \mathbf{n}} \hbar \omega_{\mathbf{n}} \hat{a}_\lambda^\dagger(\mathbf{n}) \hat{a}_\lambda(\mathbf{n}), \quad (3.10a)$$

$$\hat{\mathbf{P}}_{\text{rad}} = \sum_{\lambda, \mathbf{n}} \hbar \mathbf{k}_{\mathbf{n}} \hat{a}_\lambda^\dagger(\mathbf{n}) \hat{a}_\lambda(\mathbf{n}). \quad (3.10b)$$

In the quantum theory of the radiation field the annihilation and creation operators are mutually non-commuting operators in view of which the *order of factors* in expressions of the type (3.10) becomes important. To this concern we shall introduce the useful concept of an operator written in *normal form* as well as the concept of the *normal product* of operators [ see N.N. Bogoliubov & D.V. Shirkov (1960): *Introduction to the theory of quantized fields*, Interscience Publishers, New York, pp. 103–105 ]. The normal form of an operator involving products of creation and annihilation operators is said to be the form in which in each term all the creation operators  $\hat{a}_\lambda^\dagger(\mathbf{n})$  are written to the left of all the annihilation operators  $\hat{a}_\lambda(\mathbf{n})$ . We consider an example. We write down in normal form the

product of the two operators

$$\begin{aligned}
\widehat{F}(x)\widehat{G}(y) &\equiv \sum_{\lambda,\mathbf{n}} \left\{ [f_{\mathbf{n}}^{\lambda}(x)]^* \widehat{a}_{\lambda}^{\dagger}(\mathbf{n}) + f_{\mathbf{n}}^{\lambda}(x) \widehat{a}_{\lambda}(\mathbf{n}) \right\} \\
&\times \sum_{\sigma,\mathbf{m}} \left\{ [g_{\mathbf{m}}^{\sigma}(y)]^* \widehat{a}_{\sigma}^{\dagger}(\mathbf{m}) + g_{\mathbf{m}}^{\sigma}(y) \widehat{a}_{\sigma}(\mathbf{m}) \right\} \\
&= \sum_{\lambda,\mathbf{n}} \sum_{\sigma,\mathbf{m}} [f_{\mathbf{n}}^{\lambda}(x) g_{\mathbf{m}}^{\sigma}(y)]^* \widehat{a}_{\lambda}^{\dagger}(\mathbf{n}) \widehat{a}_{\sigma}^{\dagger}(\mathbf{m}) + \text{h.c.} \\
&+ \sum_{\lambda,\mathbf{n}} \sum_{\sigma,\mathbf{m}} [f_{\mathbf{n}}^{\lambda}(x)]^* g_{\mathbf{m}}^{\sigma}(y) \widehat{a}_{\lambda}^{\dagger}(\mathbf{n}) \widehat{a}_{\sigma}(\mathbf{m}) \\
&+ \sum_{\lambda,\mathbf{n}} \sum_{\sigma,\mathbf{m}} f_{\mathbf{n}}^{\lambda}(x) [g_{\mathbf{m}}^{\sigma}(y)]^* \widehat{a}_{\sigma}^{\dagger}(\mathbf{m}) \widehat{a}_{\lambda}(\mathbf{n}) + \sum_{\lambda,\mathbf{n}} f_{\mathbf{n}}^{\lambda}(x) [g_{\mathbf{n}}^{\lambda}(y)]^* .
\end{aligned} \tag{3.11}$$

The sum of terms not involving any ordinary  $c$ -number functions is called the normal product of the original operators. The normal product may also be defined as the original product reduced to its normal form with all the commutator functions being taken equal to zero in the process of reduction. The normal product of the operators  $\widehat{F}(x)\widehat{G}(y)$  is denoted by the symbol

$$: \widehat{F}(x)\widehat{G}(y) : \tag{3.12}$$

We now agree by definition to express all dynamical variables which depend quadratically upon operators with the same arguments, such as the energy, momentum and angular momentum of the radiation fields, in the form of normal products. For example, we shall write the energy-momentum of the radiation quantized field in the form

$$\widehat{H}_{\text{rad}} = \frac{1}{8\pi} \int_V d^3r [ : \mathbf{E}(t, \mathbf{r}) \cdot \mathbf{E}(t, \mathbf{r}) : + : \mathbf{B}(t, \mathbf{r}) \cdot \mathbf{B}(t, \mathbf{r}) : ] \tag{3.13a}$$

$$\widehat{\mathbf{P}}_{\text{rad}} = \frac{1}{4\pi c} \int_V d^3r : \mathbf{E}(t, \mathbf{r}) \times \mathbf{B}(t, \mathbf{r}) : \tag{3.13b}$$

Now, if we keep the definition of the vacuum state to be

$$\widehat{a}_{\lambda}(\mathbf{n})|0\rangle \equiv 0 \equiv \langle 0|\widehat{a}_{\lambda}^{\dagger}(\mathbf{n}) \quad \forall \lambda = 1, 2, \quad \forall \mathbf{n} \in \mathbf{Z}^3 \tag{3.14}$$

it follows that the expectation values of all the dynamical variables vanish for the vacuum state, *e.g.*,

$$\langle 0 | \widehat{H}_{\text{rad}} | 0 \rangle \equiv 0 \equiv \langle 0 | \widehat{\mathbf{P}}_{\text{rad}} | 0 \rangle, \quad \textit{et cetera} . \quad (3.15)$$

By this method we exclude from the theory at the outset pseudo-physical quantities of the type of the zero-point energy, zero-point momentum, etc., which usually arise in the process of the quantization of the field theories.

The quantization of the free radiation field gives rise to the concept of *photons*. As a matter of fact, it appears to be clear that the non-negative operators  $\widehat{a}_\lambda^\dagger(\mathbf{n})\widehat{a}_\lambda(\mathbf{n})$  do possess integer non-negative eigenvalues  $N_\lambda(\mathbf{n}) = 0, 1, 2, \dots$  which are interpreted as the *numbers of photons* of a given polarization  $\lambda$ , a given tern of wave numbers  $\mathbf{n}$  and a given energy  $\hbar\omega_{\mathbf{n}}$ . The hamiltonian operator turns out to be positive definite and from the canonical commutation relations (3.6) we can readily derive the eigenvalues and the eigenstates of  $\widehat{H}_{\text{rad}}$  : namely,

$$E(\{N_\lambda(\mathbf{n})\}) = \sum_{\lambda, \mathbf{n}} \hbar\omega_{\mathbf{n}} N_\lambda(\mathbf{n}), \quad N_\lambda(\mathbf{n}) = 0, 1, 2, \dots \quad (3.16)$$

The setting up of the eigenstates leads to the well known construction of the so called Fock space of photons, in a very close analogy with what it has been done for phonons. Actually, in order to describe  $N$ -photon states, let us consider a set of photon numbers  $\{N_\lambda(\mathbf{n}) = 0, 1, 2, \dots \mid \lambda = 1, 2, \mathbf{n} \in \mathbf{Z}^3\}$  such that  $\sum_{\lambda, \mathbf{n}} N_\lambda(\mathbf{n}) = N$ . Then the generic  $N$ -photon normalized energy eigenstate can be written as

$$|\{N_\lambda(\mathbf{n})\}\rangle_N := \prod_{\lambda, \mathbf{n}} [N_\lambda(\mathbf{n})!]^{-1/2} [a_\lambda^\dagger(\mathbf{n})]^{N_\lambda(\mathbf{n})} |0\rangle \quad (3.17)$$

which satisfies

$$\widehat{H}_{\text{rad}} |\{N_\lambda(\mathbf{n})\}\rangle_N = E_N(\{N_\lambda(\mathbf{n})\}) |\{N_\lambda(\mathbf{n})\}\rangle_N \quad (3.18)$$

$${}_M \langle \mathbf{m} \sigma | \lambda \mathbf{n} \rangle_N = \delta_{MN} \delta_{\lambda_1 \sigma_1} \delta_{\mathbf{n}_1 \mathbf{m}_1} \delta_{\lambda_2 \sigma_2} \delta_{\mathbf{n}_2 \mathbf{m}_2} \cdots \delta_{\lambda_N \sigma_M} \delta_{\mathbf{n}_N \mathbf{m}_M} . \quad (3.19)$$

The 1–photon wave function in the space–time coordinate representation is defined in terms of the matrix elements of the vector potential

$$\mathbf{f}_{\mathbf{n}}^{\lambda}(x) := \langle 0 | \widehat{\mathbf{A}}(x) | \lambda \mathbf{n} \rangle / \sqrt{2\hbar c} = L^{-3/2} (2k_0)^{-1/2} \mathbf{e}_{\lambda}(\mathbf{n}) \exp\{-ik \cdot x\} \quad (3.20)$$

and it turns out to be normalized according to the relativistic scalar product

$$\langle \mathbf{f}_{\mathbf{m}}^{\sigma} | \mathbf{f}_{\mathbf{n}}^{\lambda} \rangle := i \int_V d^3x [\partial_0 \mathbf{f}_{\mathbf{n}}^{\lambda}(x)] \cdot [\mathbf{f}_{\mathbf{m}}^{\sigma}(x)]^* + \text{c.c.} = \delta_{\lambda\sigma} \delta_{\mathbf{nm}} . \quad (3.21)$$

The normalized  $N$ –photon energy eigenfunctions in the coordinates representation can be readily obtained in the usual completely symmetric form

$$\begin{aligned} \mathbf{f}_N(x_1, x_2, \dots, x_N) &= \frac{1}{\sqrt{N!}} \sum_{[\text{Perm}]} \{ \mathbf{f}_{\mathbf{n}_1}^{\lambda_1}(P_1) \mathbf{f}_{\mathbf{n}_2}^{\lambda_2}(P_2) \dots \mathbf{f}_{\mathbf{n}_N}^{\lambda_N}(P_N) \} \\ &:= \langle x_1 x_2 \dots x_N | \lambda_1 \mathbf{n}_1 \lambda_2 \mathbf{n}_2 \dots \lambda_N \mathbf{n}_N \rangle \end{aligned} \quad (3.22)$$

where [Perm] denotes as usual the generic permutation  $(1, 2, \dots, N) \mapsto (P_1, P_2, \dots, P_N)$  of the  $N$  space–time points  $x_1, x_2, \dots, x_N$ .

Furthermore, we can write the generic normalized element of the  $N$ –photon completely symmetric Hilbert space (the closure of the symmetric product of 1–photon Hilbert spaces)

$$\mathcal{H}_N^{(+)} := \overbrace{S\{\mathcal{H}_1 \otimes \mathcal{H}_1 \otimes \dots \otimes \mathcal{H}_1\}}_{N \text{ times}}$$

in the form

$$|\varphi_N\rangle := \sum_{\lambda_1, \mathbf{n}_1} \sum_{\lambda_2, \mathbf{n}_2} \dots \sum_{\lambda_N, \mathbf{n}_N} C(\lambda_1, \mathbf{n}_1; \lambda_2, \mathbf{n}_2; \dots; \lambda_N, \mathbf{n}_N) |\{N_{\lambda}(\mathbf{n})\}\rangle_N \quad (3.23)$$

with

$$\sum_{\lambda_1, \mathbf{n}_1} \sum_{\lambda_2, \mathbf{n}_2} \dots \sum_{\lambda_N, \mathbf{n}_N} |C(\lambda_1, \mathbf{n}_1; \lambda_2, \mathbf{n}_2; \dots; \lambda_N, \mathbf{n}_N)|^2 = 1 . \quad (3.24)$$

To end up, we are now able to write the generic normalized element of the Fock space of the photon states

$$\mathcal{F}_{\text{photons}} \equiv \mathbf{C} \oplus \mathcal{H}_1 \oplus \mathcal{H}_2^{(+)} \oplus \dots \oplus \mathcal{H}_N^{(+)} \dots \quad (3.25)$$

in the form

$$|\Phi\rangle = \sum_{N=0}^{\infty} C_N |\varphi_N\rangle, \quad \sum_{N=0}^{\infty} |C_N|^2 = 1 \quad (3.26)$$

which summarizes our explicit construction of the photon states, the structure of which is characterized by the canonical quantum algebra (3.8) and the hamiltonian operator (3.10).

Actually, from the classical expression (3.7) of the hamiltonian function and from the corresponding expression (3.16) for the eigenvalues of the quantum hamiltonian operator (3.10), it appears to be clear that the energy of the radiation field enclosed in a box, usually called the *black body radiation*, may be considered as arising from an assembly of an infinite number of *non-interacting* one dimensional harmonic oscillators, the characteristic frequencies of which are given by  $\omega_{\mathbf{n}} = 2\pi c|\mathbf{n}|/L$ . We can say as well that the quantum mechanical treatment of the normal modes of the black body radiation just leads to the picture of an *ideal gas of free photons* enclosed within the black box.

The statistical thermodynamics of the black body radiation was firstly discovered by Maximilian Karl Ernst Ludwig Planck (Kiel 23.4.1858 – Gottinga 4.10.1947, strong oppositor of the nazist regime and of antisemitism) *Verhandl. Deut. Physik Ges.* **2** (1900) 202, 237. It can be better formulated in terms of the canonical ensemble, as it has been done at the end of §IV.4. The quantization of the black body radiation normal modes leads immediately to the canonical quantum partition function

$$\begin{aligned} Z_{\text{rad}}(T, V) &= \text{Tr} \exp\{-\beta \hat{H}_{\text{rad}}\} \\ &= \prod_{\lambda, \mathbf{n}} \sum_{N_{\lambda}(\mathbf{n})=0}^{\infty} \exp\{-N_{\lambda}(\mathbf{n})\beta \hbar \omega_{\mathbf{n}}\} \\ &= \prod_{\mathbf{n}} (1 - \exp\{-\beta \hbar \omega_{\mathbf{n}}\})^{-2} \end{aligned} \quad (3.27)$$

whence the Helmholtz free energy readily follows

$$F_{\text{rad}}(T, V) = 2kT \sum_{\mathbf{n}} \ln(1 - \exp\{-\beta \hbar \omega_{\mathbf{n}}\}) \quad (3.28)$$



together with the internal energy

$$U_{\text{rad}}(T, V) = \sum_{\mathbf{n}} \frac{2\hbar\omega_{\mathbf{n}}}{\exp\{\beta\hbar\omega_{\mathbf{n}}\} - 1} \quad (3.29)$$

Under the assumption that the volume of the black box is sufficiently large so that the boundary effects become negligible, we can make as usual the transition to the *continuum limit* and the customary replacements  $\sum_{\mathbf{n}} \mapsto \int d^3n$ . Taking into account that the photon dispersion relation depend solely upon the absolute value of the wave numbers we can definitely set

$$2 \int d^3n = \frac{V}{\pi^2 c^3} \int_0^\infty d\omega \omega^2 \quad (3.30)$$

and consequently we find

$$\begin{aligned} F_{\text{rad}}(T, V) &= \frac{V k T}{\pi^2 c^3} \int_0^\infty d\omega \omega^2 \ln(1 - \exp\{-\beta\hbar\omega\}) \\ &= -\frac{V(kT)^4}{3\pi^2 \hbar^3 c^3} \int_0^\infty \frac{x^3 dx}{e^x - 1}; \end{aligned} \quad (3.31)$$

$$\begin{aligned} U_{\text{rad}}(T, V) &= \frac{V}{\pi^2 c^3} \int_0^\infty \frac{\hbar\omega^3 d\omega}{\exp\{\beta\hbar\omega\} - 1} \\ &= \frac{V(kT)^4}{\pi^2 \hbar^3 c^3} \int_0^\infty \frac{x^3 dx}{e^x - 1}. \end{aligned} \quad (3.32)$$

The integrals of the above kind can be calculated as follows. We have

$$\int_0^\infty \frac{x^{s-1} dx}{e^x - 1} = \Gamma(s) \zeta(s) \quad (3.33)$$

where  $\zeta(s) = \sum_{n=1}^\infty n^{-s}$  is the *Riemann's  $\zeta$ -function*. For  $s = 2n$  we find

$$\int_0^\infty \frac{x^{2n-1} dx}{e^x - 1} = \frac{(2\pi)^{2n} B_n}{4n} \quad (3.34)$$

and the first *Bernoulli's numbers* are

$$B_1 = \frac{1}{6}; \quad B_2 = \frac{1}{30}; \quad B_3 = \frac{1}{42}; \quad B_4 = \frac{1}{30}. \quad (3.35)$$

As a consequence we definitely get

$$F_{\text{rad}}(T, V) = - \frac{4\sigma}{3c} VT^4 = - \frac{1}{3} U_{\text{rad}}(T, V), \quad (3.36)$$

where the coefficient  $\sigma$  is called the *Stefan–Boltzmann’s constant* and takes the value

$$\sigma = \frac{\pi^2 k^4}{60 \hbar^3 c^2} = 5.670\,400(40) \times 10^{-8} \text{ W m}^{-2} \text{ }^\circ\text{K}^{-4}. \quad (3.37)$$

The entropy is given by

$$S_{\text{rad}}(T, V) = - \left( \frac{\partial F_{\text{rad}}}{\partial T} \right)_V = \frac{16\sigma}{3c} VT^3, \quad (3.38)$$

whereas the heat capacity of the black body radiation at the thermodynamic equilibrium reads

$$C_V = \left( \frac{\partial U_{\text{rad}}}{\partial T} \right)_V = \frac{16\sigma}{c} VT^3. \quad (3.39)$$

Finally, the black body radiation pressure at the thermal equilibrium will be given by

$$p_{\text{rad}} = - \left( \frac{\partial F_{\text{rad}}}{\partial V} \right)_T = \frac{4\sigma}{3c} T^4, \quad V p_{\text{rad}} = \frac{1}{3} U_{\text{rad}}(T, V), \quad (3.40)$$

whence it immediately follows that the Gibbs free enthalpy and the chemical potential of the radiation do exactly vanish.

The average number of photons with a given frequency  $\omega$  at the thermodynamical equilibrium is provided by the Bose–Einstein distribution: namely,

$$\langle N_\omega \rangle_T = \frac{1}{\exp\{\beta \hbar \omega\} - 1}, \quad (3.41)$$

so that the average number of photons inside the black box at the thermal equilibrium at the temperature  $T$  will be expressed by

$$\begin{aligned} \langle N \rangle_T &= \frac{V}{\pi^2 c^3} \int_0^\infty \frac{\omega^2 d\omega}{\exp\{\beta \hbar \omega\} - 1} \\ &= \frac{V(kT)^3}{\pi^2 \hbar^3 c^3} \int_0^\infty \frac{x^2 dx}{e^x - 1} = \frac{2\zeta(3)}{\pi^2} \left( \frac{kT}{\hbar c} \right)^3 V. \end{aligned} \quad (3.42)$$

#### IX.4. Bose–Einstein condensation.

In continuation of Section §VI.5. we shall now investigate in more detail the physical behaviour of an ideal system of identical particles obeying the Bose–Einstein statistics. In particular, we shall here below investigate the situation in which the effects of quantum statistics, arising from the indistinguishability of the particles, do assume an increasingly important role. This means that the temperature  $T$  and the particle density  $n$  of the system do not conform to the criterion  $nh^3(2\pi mkT)^{-3/2} \ll 1$ .

We obtained in Section §VI.5. the average number of particles as well as the thermodynamic potentials in the quantum grand–canonical ensemble for an ideal Bose–Einstein system of identical molecules. In particular we aim to consider the parametric equations for the average number of molecules and the internal energy of the system, the parameter being as usual the chemical potential  $\mu$  : namely,

$$N(\mu, T; \alpha) = \sum_{i=0}^{\infty} \frac{d_i \exp\{\beta(\mu - \varepsilon_i)\}}{1 - \exp\{\beta(\mu - \varepsilon_i)\}}, \quad (4.1a)$$

$$U(\mu, T; \alpha) = \sum_{i=0}^{\infty} \varepsilon_i \frac{d_i \exp\{\beta(\mu - \varepsilon_i)\}}{1 - \exp\{\beta(\mu - \varepsilon_i)\}}, \quad (4.1b)$$

where  $\varepsilon_i$ ,  $d_i$  indicate the energy levels and degeneracies respectively of the single–molecule hamiltonian operator (we suppose  $d_0 = 1$ ,  $d_i < \infty \forall i \in \mathbf{N}$ ). We recall that the energy levels and degeneracies of the single–molecule hamiltonian operator do in general depend upon the control parameters  $\alpha = \alpha_1, \alpha_2, \dots, \alpha_r$ , which include the background fields and the specific labels of the boundary conditions fulfilled by the wave functions, owing to the presence of the container walls.

Now, it is also worth while to recall that  $\mu < \varepsilon_0$ , in order that all the mean numbers of molecules allocated in the single–molecule energy levels at the thermal equilibrium are non–negative. It is clear that as long as chemical potential becomes closer and closer to

the ground state energy  $\varepsilon_0$  the first term in the series in eq. (4.1b) might become as big as the whole sum of all the other ones. As a consequence, it is convenient to rewrite eq. (4.1a) in terms of the fugacity  $z$ , with  $0 \leq z < z_0$  : namely,

$$N = \frac{z}{z_0 - z} + N_e(z, T; \alpha) , \quad (4.2)$$

in which we have set  $z_0 := \exp\{\beta\varepsilon_0\}$  and we naturally identify

$$N_e(z, T; \alpha) := \sum_{i=1}^{\infty} \frac{z d_i \exp\{-\beta\varepsilon_i\}}{1 - z \exp\{-\beta\varepsilon_i\}} . \quad (4.3)$$

It appears manifest that  $N_e(z, T; \alpha)$  does represent the mean number of molecules distributed among all the excited eigenstates of the single-molecule hamiltonian operator at the thermodynamic equilibrium at the absolute temperature  $T$ . Let us now increase the chemical potential and/or decrease the temperature in such a way that the fugacity could reach its face value  $z_0$ . In so doing the mean number of molecules necessarily increase, since  $N$  turns out to be a monotonically increasing function of the fugacity  $0 \leq z < z_0$ . Suppose that we have

$$\lim_{z \uparrow z_0} N_e(z, T; \alpha) = N_e(z_0, T; \alpha) := N_*(T; \alpha) < \infty . \quad (4.4)$$

In such a situation of thermodynamic equilibrium, as soon as  $N > N_*$ , since all the excited states are fully occupied, *a finite number of molecules is necessarily accomodated in the single-molecule ground state*. This is just the phenomenon of the Bose-Einstein condensation [ S.N. Bose (1924) *Z. Phys.* **26**, 178; A. Einstein (1924) *Sitzber. Kgl. Preuss. Akad. Wiss.* 261; (1925) *ibid.* 3 ]. If we set

$$N - N_* := N_0 \geq 0 , \quad (4.5)$$

we can write the particle number equation in the form

$$N = \frac{z}{z_0 - z} + N_e(z, T; \alpha) , \quad \text{iff } 0 \leq z < z_0 ; \quad (4.6a)$$

$$N = N_0 + N_*(T; \alpha) , \quad \text{iff } z = z_0 . \quad (4.6b)$$

It is worth while to remark that when  $kT < \varepsilon_1 - \varepsilon_0$  all the molecules are actually accomodated in the ground state. As a matter of fact, from the expression (4.3) we can easily check that indeed

$$\lim_{T \downarrow 0} N_e(z, T; \alpha) = 0, \quad \forall z \in [0, z_0]. \quad (4.7)$$

On the one hand, at a given temperature  $T$  and for a given assignement of the control parameters  $\alpha$ , the number  $N_c = N_*(T; \alpha)$  is the *critical particle number* above which the Bose–Einstein condensate is present. On the other hand, for a given average number of molecules  $N$  and for a given assignement of the control parameters  $\alpha$ , the solution of the equation

$$N = N_*(T; \alpha) \quad \Leftrightarrow \quad T = T_c(N; \alpha) \quad (4.8)$$

allows to find the *critical temperature*  $T_c$  below which the Bose–Einstein condensate is present. In this case it is also customary to introduce the so called *order parameter*

$$\phi(T; \alpha) := \frac{N_0}{N} = 1 - \nu_*(T; \alpha) := 1 - \frac{N_*}{N} \quad (4.9)$$

which represents the average *fraction of molecules in the Bose–Einstein condensate*, whereas  $\nu_*(T; \alpha)$  does represent the mean fraction of molecules in the *normal Bose–Einstein gas*, that means the average number of molecules distributed among the excited single–particle states. Obviously, it turns out that  $0 \leq \phi(T; \alpha) \leq 1$  and more specifically

$$\phi(T; \alpha) = \begin{cases} 0, & \text{iff } T \geq T_c; \\ 1, & \text{iff } T \downarrow 0. \end{cases} \quad (4.10)$$

It follows that, for a given average number of molecules  $N$  and for a given assignement of the control parameters  $\alpha$ , above the critical temperature  $T_c$ , *i.e.*  $z < z_0$ , we have only the normal gas and the order parameter is equal to zero. Conversely, below the critical

temperature  $T_c$ , *i.e.*  $z = z_0$ , the system consists of a mixture of normal gas and condensate and a non-vanishing order parameter arises.

*Below the critical temperature the system is no longer homogeneous, albeit it consists of two co-existing phases. The critical temperature labels thereby the onset of a phase transition in which the ideal boson system becomes a mixture.*

Actually we can find general conditions under which the Bose–Einstein condensation takes place. This is the content of the following

**Theorem.**

Suppose the single-particle energy spectrum of an ideal boson gas satisfies the following conditions:

- (i) there is a gap between the fundamental and the first excited energy levels, *i.e.*  $\varepsilon_1 - \varepsilon_0 = \Delta > 0$ ;
- (ii) the single-particle partition function is finite, *i.e.*  $Z \equiv \sum_{n=0}^{\infty} d_n \exp(-\beta\varepsilon_n) < \infty$ ,  $d_n$  being the finite degeneracy of the  $n$ -th eigenvalue of the single-particle hamiltonian.

Then this gas displays Bose–Einstein condensation at finite temperature.

*Proof.*

If  $\mu < \varepsilon_0$ , the number of particles in the excited states is bounded from above by

$$N_e = \sum_{n=1}^{\infty} \frac{d_n \exp[-\beta(\varepsilon_n - \mu)]}{1 - \exp[-\beta(\varepsilon_n - \mu)]} \leq \frac{\exp(\beta\mu)}{1 - \exp[-\beta(\varepsilon_1 - \mu)]} \sum_{n=1}^{\infty} d_n \exp(-\beta\varepsilon_n) . \quad (4.11)$$

Therefore

$$\lim_{\mu \rightarrow \varepsilon_0} N_e \leq \frac{\exp(\beta\varepsilon_0)}{1 - \exp(-\beta\Delta)} [Z - d_0 \exp(-\beta\varepsilon_0)] < \infty , \quad (4.12)$$

since, by hypothesis,  $Z$  and  $d_0$  are finite and  $\Delta > 0$ .

*Q.E.D.*

We notice that the above statement may be generalized to some cases in which part of the spectrum is continuous or there are infinitely degenerate energy levels. This is done

under the suitable introduction of the density of particles in the excited states and of the single-particle partition function per unit volume, as we shall see in the sequel.

As far as the internal energy is concerned, for a given average number of particles  $N$  the above reasoning shows us that in the homogeneous phase above  $T_c$  we have

$$U(z, T; \alpha) = \frac{z\varepsilon_0}{z_0 - z} + \sum_{i=1}^{\infty} \frac{z\varepsilon_i d_i \exp\{-\beta\varepsilon_i\}}{1 - z \exp\{-\beta\varepsilon_i\}}, \quad 0 \leq z < z_0 \quad (4.13)$$

whereas in the mixed phase below  $T_c$  we can write

$$U(T; \alpha) = N_0 \varepsilon_0 + \sum_{i=1}^{\infty} \frac{z_0 \varepsilon_i d_i \exp\{-\beta\varepsilon_i\}}{1 - z_0 \exp\{-\beta\varepsilon_i\}}, \quad z = z_0. \quad (4.14)$$

Notice that we have consistently

$$\lim_{T \downarrow 0} U(T; \alpha) = N \varepsilon_0. \quad (4.15)$$

Furthermore, the heat capacity, the entropy and thereby any other thermodynamic quantity of the ideal boson system can be obtained from the usual formulae

$$C_\alpha(z, T) = \left( \frac{\partial U}{\partial T} \right)_{z, \alpha}, \quad S(z, T; \alpha) = \int_0^T \frac{d\tau}{\tau} C_\alpha(z, \tau). \quad (4.16)$$

Bose–Einstein condensation was firstly observed in 1995 in a remarkable series of experiments on vapours of rubidium [ M.H. Anderson, J.R. Ensher, M.R. Matthews, C.E. Wieman, E.A. Cornell (1995) *Science* **269**, 198 ] and of sodium [ K. Davis, M.–O. Mewes, M.R. Andrews, N.J. van Druten, D.S. Durfee, D.M. Kurn, W. Ketterle (1995) *Phys. Rev. Lett.* **75**, 3969 ] in which the atoms were confined in magnetic traps and cooled down to extremely low temperatures of the order of fractions of microkelvins. The first evidence for condensation emerged from time of flight measurements. The atoms were left to expand by switching off the confining trap and then imaged with optical methods. A sharp peak in

the velocity distribution was then observed below a certain critical temperature, providing a clear signature for the Bose–Einstein condensation.

Though the experiments in 1995 on the alkalis should be considered as a milestone in the history of the Bose–Einstein condensation, we have admittedly to recall that the experimental and theoretical research on this unique phenomenon predicted by quantum statistical mechanics is much older and has involved different areas of physics. In particular, from the very beginning, superfluidity in liquid helium was considered by F. London (1938) *Nature* **141**, 643, as a possible manifestation of the Bose–Einstein condensation. Evidence for Bose–Einstein condensation in helium later emerged from the analysis of the momentum distribution of the atoms measured in neutron–scattering experiments [ P. Sokol (1995) in *Bose–Einstein condensation*, edited by A. Griffin, D.W. Snoke and S. Stringari, Cambridge University Press, Cambridge, p. 51 ].

Alkali atoms are well suited to laser–based methods because their optical transitions can be excited by available lasers and because they have a favourable internal energy levels structure for cooling to very low temperatures. Once they are trapped, the temperature can be further lowered by evaporative cooling. The suitable combination of the laser and evaporative cooling techniques for alkali atoms eventually allowed experimentalists to reach the temperatures and densities required to obtain the Bose–Einstein condensation. As an example, in one of the first experiments [ J.R. Ensher, D.S. Jin, M.R. Matthews, C.E. Wieman, E.A. Cornell (1996) *Phys. Rev. Lett.* **77**, 4984 ] the critical temperature was of the order  $3 \times 10^{-7}$  °K with 40 000 atoms in the trap. It is worth while to remark that in this conditions the equilibrium state of the system would be in the solid phase. As a consequence, in order to observe the Bose–Einstein condensation, it is necessary to keep the system in a metastable vapour phase for a sufficiently long time. This is possible



because two- and three-body collisions are rare events in a very dilute and very cold gaseous system, so that its lifetime is large enough (few seconds) to carry out experiments.

One of the most relevant features of all the trapped boson gases is that they are spatially inhomogeneous and contain a finite number of particles, typically ranging from a few thousands to several millions. In most practical cases, the confining traps are very well approximated by *harmonic potential*. The trapping frequency  $\omega$  just provides the characteristic length  $a = \sqrt{\hbar/m\omega}$ , of the order of few microns in the available samples, that represents the length scale upon which the spatial density variations do actually occur. This is the main difference with respect to the superfluid helium in which the spatial density variations appear on the much smaller scale provided by the mean interatomic distance. The fact that the trapped vapours are highly inhomogeneous has the very important consequence that the Bose-Einstein condensation shows up in coordinate space and not in the momentum space as it happens in the superfluid  $^4\text{He}$ .

### IX.5. Ideal boson gas in a harmonic trap.

An important feature characterizing the available magnetic traps for alkali atoms is that the confining potential can be safely approximated by the harmonic form

$$V(\mathbf{r}) = \frac{m}{2} (\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2) . \quad (5.1)$$

The spectrum of the single-particle hamiltonian operator is notoriously given by

$$E_{n_x, n_y, n_z} = \hbar(\omega_x n_x + \omega_y n_y + \omega_z n_z) + \frac{1}{2} \hbar(\omega_x + \omega_y + \omega_z) , \quad (5.2)$$

$$n_x + 1 \in \mathbf{N} , \quad n_y + 1 \in \mathbf{N} , \quad n_z + 1 \in \mathbf{N} ,$$

The ground state of  $N$  non-interacting bosons confined by the potential (5.1) is obtained by putting all the particles in the lowest single-particle state  $n_x = n_y = n_z = 0$  so that

$$\Phi_0(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \prod_{i=1}^N \left( \frac{m\bar{\omega}}{\pi\hbar} \right)^{3/4} \exp \left\{ -\frac{m}{2\hbar} (\omega_x x_i^2 + \omega_y y_i^2 + \omega_z z_i^2) \right\} , \quad (5.3)$$

where we have introduced the average angular frequency trap  $\bar{\omega} := (\omega_x \omega_y \omega_z)^{1/3}$ . The spatial density distribution of the particles becomes

$$n(x, y, z) = N \left( \frac{m\bar{\omega}}{\pi\hbar} \right)^{3/2} \exp \left\{ -\frac{m}{2\hbar} (\omega_x x^2 + \omega_y y^2 + \omega_z z^2) \right\} \quad (5.4)$$

and it grows like  $N$ , whereas its size is fixed by the characteristic length  $a = (\hbar/m\bar{\omega})^{1/2}$  which corresponds to the average width of the normalized gaussian in eq. (5.4). In the available experiments the above characteristic length is of the order of the micron. At any finite temperature only a fraction of the atoms occupy the lowest state, the rest being thermally distributed among the excited states.

At the equilibrium temperature  $T$  the mean number of particles and the internal

energy will be given by

$$\begin{aligned}
N &= \sum_{n_x=0}^{\infty} \sum_{n_y=0}^{\infty} \sum_{n_z=0}^{\infty} \frac{\exp\{\beta\mu - \beta\epsilon_0 - \beta\hbar(\omega_x n_x + \omega_y n_y + \omega_z n_z)\}}{1 - \exp\{\beta\mu - \beta\epsilon_0 - \beta\hbar(\omega_x n_x + \omega_y n_y + \omega_z n_z)\}} \\
&= \frac{\exp\{\beta\mu - \beta\epsilon_0\}}{1 - \exp\{\beta\mu - \beta\epsilon_0\}} + N_e, \quad \mu < \epsilon_0 := \hbar(\omega_x + \omega_y + \omega_z)/2, \\
U &= \sum_{n_x=0}^{\infty} \sum_{n_y=0}^{\infty} \sum_{n_z=0}^{\infty} E_{n_x, n_y, n_z} [\exp\{-\beta\mu + \beta E_{n_x, n_y, n_z}\} - 1]^{-1} \\
&= \frac{\epsilon_0 \exp\{\beta\mu - \beta\epsilon_0\}}{1 - \exp\{\beta\mu - \beta\epsilon_0\}} + \sum_{n_x=0}^{\infty} \sum_{n_y=0}^{\infty} \sum_{n_z=0}^{\infty} \frac{\hbar(\omega_x n_x + \omega_y n_y + \omega_z n_z)}{\exp\{-\beta\mu + \beta E_{n_x, n_y, n_z}\} - 1}.
\end{aligned} \tag{5.5}$$

If the conditions are such that  $\hbar\bar{\omega} \ll kT$ , which corresponds to the *quasi*-classical approximation, we can perform the transition to the *continuum limit* and replace the series with integrals: namely,

$$\sum_{n=0}^{\infty} \mapsto \int_0^{\infty} dn.$$

As a consequence, we can rewrite the mean number of particles in the excited states in the *quasi*-classical approximation in the form

$$\begin{aligned}
N_e &\approx \int_0^{\infty} dn_x \int_0^{\infty} dn_y \int_0^{\infty} dn_z \frac{\exp\{\beta\mu - \beta\epsilon_0 - \beta\hbar(\omega_x n_x + \omega_y n_y + \omega_z n_z)\}}{1 - \exp\{\beta\mu - \beta\epsilon_0 - \beta\hbar(\omega_x n_x + \omega_y n_y + \omega_z n_z)\}} \\
&= \sum_{j=0}^{\infty} \exp\{\beta(\mu - \epsilon_0)(j+1)\} \prod_{i=x,y,z} \int_0^{\infty} dn \exp\{-\beta\hbar\omega_i n(j+1)\} \\
&= \sum_{j=1}^{\infty} \left(\frac{kT}{j\hbar\bar{\omega}}\right)^3 \exp\{j\beta(\mu - \epsilon_0)\} = \left(\frac{kT}{\hbar\bar{\omega}}\right)^3 g_3(z_*),
\end{aligned} \tag{5.6}$$

where we have set

$$z_* \equiv \exp\{\beta(\mu - \epsilon_0)\} = z \exp\{-3\beta\hbar\bar{\omega}/2\} \tag{5.7}$$

and we have introduced the *Bose–Einstein functions of order s*: namely,

$$g_s(z) \equiv \sum_{j=1}^{\infty} \frac{z^j}{j^s}, \quad \Re s > 0, \quad 0 \leq z < 1. \tag{5.8}$$

In conclusion we can definitely write

$$N = N_0 + N_e = \frac{z_*}{1 - z_*} + \left(\frac{kT}{\hbar\bar{\omega}}\right)^3 g_3(z_*), \quad 0 \leq z_* < 1. \tag{5.9}$$

In a quite similar way we shall obtain the expression of the internal energy in the *quasi*-classical approximation: namely,

$$\begin{aligned}
U &\approx \frac{z_* \epsilon_0}{1 - z_*} + \sum_{j=1}^{\infty} z_*^j \int_0^{\infty} dn_x \hbar \omega_x n_x \exp \{-\beta \hbar j \omega_x n_x\} \times \\
&\times \int_0^{\infty} dn_y \exp \{-\beta \hbar j \omega_y n_y\} \int_0^{\infty} dn_z \exp \{-\beta \hbar j \omega_z n_z\} + \dots \quad (5.10) \\
&= \frac{z_* \epsilon_0}{1 - z_*} + 3kT \left( \frac{kT}{\hbar \bar{\omega}} \right)^3 g_4(z_*), \quad 0 \leq z_* < 1.
\end{aligned}$$

Now we find

$$\lim_{z_* \uparrow 1} N_e(z_*, T, \bar{\omega}) = \left( \frac{kT}{\hbar \bar{\omega}} \right)^3 \zeta(3) := N_*(T, \bar{\omega}) < \infty \quad (5.11)$$

where  $\zeta(s) := \sum_{j=1}^{\infty} j^{-s}$ ,  $\Re s > 1$  is the *Riemann zeta function*. From eq. (4.8) it follows that, for a given average number of particles  $N \geq N_*$ , the critical temperature is provided by

$$N_*(T_c, \bar{\omega}) = N \quad \Leftrightarrow \quad kT_c = \hbar \bar{\omega} \sqrt[3]{N/\zeta(3)} \simeq 0.94 \hbar \bar{\omega} \sqrt[3]{N}. \quad (5.12)$$

Moreover, it turns out that the order parameter can be identified with

$$\phi \equiv \frac{N_0}{N} = 1 - \frac{\zeta(3)}{N} \left( \frac{kT}{\hbar \bar{\omega}} \right)^3 = 1 - \left( \frac{T}{T_c} \right)^3. \quad (5.13)$$

In conclusion, we see that for  $z_* = 1$ , that means  $T \leq T_c$ , we can write the average number and the internal energy of the molecules in the harmonic trap in the form

$$\begin{aligned}
N &= N_0 + \zeta(3) \left( \frac{kT}{\hbar \bar{\omega}} \right)^3 \\
&= N_0 + N_*(T, \bar{\omega}), \quad (5.14)
\end{aligned}$$

$$\begin{aligned}
U &= N_0 \epsilon_0 + 3kT \left( \frac{kT}{\hbar \bar{\omega}} \right)^3 \zeta(4) \\
&= N_0 \epsilon_0 + 3N_* kT \zeta(4)/\zeta(3). \quad (5.15)
\end{aligned}$$

From the above expression of the internal energy we can readily obtain the heat capacity and the entropy below the critical temperature which read

$$C = 12Nk [\zeta(4)/\zeta(3)] \left(\frac{T}{T_c}\right)^3, \quad T \leq T_c; \quad (5.15)$$

$$S = 4Nk [\zeta(4)/\zeta(3)] \left(\frac{T}{T_c}\right)^3, \quad T \leq T_c. \quad (5.16)$$

We see that, as expected, the heat capacity and the entropy do vanish with a cubic law for  $T \downarrow 0$ , that means, *the Bose–Einstein condensate does not carry neither heat capacity nor entropy, i.e.*, the latter ones are always carried on by the normal boson vapour.

The above analysis – see in particular eq. (5.12) – shows the existence of two relevant scales of energy for the ideal Bose–Einstein gas: the transition temperature  $kT_c$  and the average level spacing  $\hbar\bar{\omega}$ , the latter being usually much smaller than the former one. In the available traps, with  $N$  ranging from a few thousand to several millions, the critical temperature is 20 to 200 times larger than the average level spacing. This means that the *quasi*–classical approximation is expected to work very well in these systems on a wide and useful range of temperatures. The frequency  $\bar{\omega}/2\pi$  is fixed by the trapping potential and ranges typically from 10 ÷ 100 Hertz: this gives  $\hbar\bar{\omega}$  of the order of the nano–kelvin. In one of the first experiments [ J.R. Ensher, D.S. Jin, M.R. Matthews, C.E. Wieman, E.A. Cornell (1996) *Phys. Rev. Lett.* **77**, 4984 ] the average level spacing was about  $9 \times 10^{-9}$  °K, corresponding to a critical temperature of about  $3 \times 10^{-7}$  °K with 40 000 atoms – see eq. (5.12). The non–interacting harmonic trap model has guided the experimentalists to the proper value of the critical temperature. In fact, the measured transition temperature was found to be very close to the ideal gas value of eq. (5.12), the occupation of the single–particle ground state being macroscopically large below the critical temperature as predicted by the order parameter cubic law of eq. (5.13).

## IX.6. Bose–Einstein condensation in momentum space.

Let us now consider an ideal boson gas of free point-like particles of mass  $m$  in the  $D$ -dimensional space,  $D = 1, 2, 3$ , enclosed in a large box of volume  $V_D$ . The single-molecule hamiltonian operator will be thereby given by

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} . \quad (6.1)$$

When spin degrees of freedom are taken into account, each eigenvalue of the hamiltonian (6.1) becomes  $(2\mathbf{S} + 1)$ -times degenerate if  $\hbar\sqrt{\mathbf{S}(\mathbf{S} + 1)}$  is the eigenvalue of the modulus of the intrinsic integer angular momentum operator.

It is quite instructive to realize that the density of the single-molecule states can also be obtained, in the present case, after transition to the so called *continuum limit* or large volume limit. To this aim, if we consider the molecules of the gas to be enclosed in a linear, square, cubic box of side  $L$  and impose, for instance, periodic boundary conditions on the wave functions – in such a way that the hamiltonian operator (6.1) turns out to be self-adjoint – then the eigenfunctions are

$$\begin{aligned} \psi_{\mathbf{n}}(\mathbf{r}) &= L^{-D/2} \exp\{i\mathbf{k} \cdot \mathbf{r}\} , \\ \mathbf{k} &= \frac{2\pi\mathbf{n}}{L} , \quad \mathbf{n} \in \mathbf{Z}^D . \end{aligned} \quad (6.2)$$

It follows therefrom that the momentum eigenvalues are given by

$$\mathbf{p} = \hbar\mathbf{k} = \frac{2\pi\hbar}{L}\mathbf{n} , \quad (6.3)$$

and, consequently, we see that in a very large box the energy and momentum spectra become nearly continuous. This means that we can safely approximate

$$\sum_{n_x=-\infty}^{+\infty} \longmapsto \frac{1}{h} \int_{-\infty}^{+\infty} dp_x \int_0^L dx , \quad \text{etc.} , \quad (6.4)$$

In conclusion, for a very large box we finally obtain the continuum limit in which

$$(2\mathbf{S} + 1) \sum_{\mathbf{n}} \mapsto \frac{2\mathbf{S} + 1}{h^D} \int_{V_D} d^D r \int d^D p . \quad (6.5)$$

If we recall that  $E = (p^2/2m) \Leftrightarrow dE = (p/m)dp \Leftrightarrow dp = (mdE/\sqrt{2mE})$  we can write

$$(2\mathbf{S} + 1) \frac{V_D}{h^D} d^D p = (2\mathbf{S} + 1) \frac{2\pi^{D/2} V_D}{h^D \Gamma(D/2)} p^{D-1} dp \quad (6.6)$$

whence it follows that the density of single-molecule states *per* unit volume is given by

$$\varrho(E, \mathbf{S}) = \frac{2\mathbf{S} + 1}{E \Gamma(D/2)} \left( \frac{2m\pi E}{h^2} \right)^{D/2} = \frac{d\tau}{dE}(E, \mathbf{S}) = \frac{D}{2} \tau(E, \mathbf{S})/E . \quad (6.7)$$

The distribution  $\tau(E, \mathbf{S})$  of the single-molecule energy eigenstates up to the energy  $E$  can also be easily obtained in terms of the Laplace anti-transform of the single-molecule partition function density. As a matter of fact, owing to translation invariance, we find the single-molecule partition function density to be

$$\begin{aligned} Z(\beta) &= (2\mathbf{S} + 1) \langle \mathbf{r} | \exp \{ -\beta \hat{\mathbf{p}}^2 / 2m \} | \mathbf{r} \rangle \\ &= \frac{2\mathbf{S} + 1}{h^3} \int d^D p \exp \left\{ -\beta \frac{p^2}{2m} \right\} = (2\mathbf{S} + 1) \left( \frac{2\pi m}{h^2 \beta} \right)^{D/2} . \end{aligned} \quad (6.8)$$

It follows therefore that, for any  $c > 0$  we get

$$\begin{aligned} \tau(E, \mathbf{S}) &= (2\mathbf{S} + 1) \left( \frac{2\pi m}{h^2} \right)^{D/2} \int_{c-i\infty}^{c+i\infty} \frac{ds}{2\pi i} s^{-1-D/2} \exp\{sE\} \\ &= \frac{2\mathbf{S} + 1}{\Gamma(1 + D/2)} \left( \frac{2m\pi E}{h^2} \right)^{D/2} , \end{aligned} \quad (6.9)$$

in agreement with eq. (6.7).

Let us study now in more detail the various thermodynamical potentials as well as the state equation for the ideal gas of non-relativistic free particles. In the present case, the single-particle ground-state just corresponds to  $E_0 = 0 = \mathbf{p}$ , *i.e.*, particles at rest somewhere within the large  $D$ -dimensional box of volume  $V_D$ . As a consequence, after

separation of the single-particle ground state contribution and taking the continuum limit for the excited states contribution, we can cast the grandpotential in the approximate form

$$\begin{aligned}\Omega(\mu, T, V_D; \mathbf{S}) &\approx - (2\mathbf{S} + 1)kT \ln(1 - z) + V_D \int_0^\infty dE \frac{\tau(E, \mathbf{S})}{\exp\{\beta(E - \mu)\} - 1} \\ &= - (2\mathbf{S} + 1)kT \{ \ln(1 - z) + V_D \lambda_T^{-D} g_{(D+1)/2}(z) \} ,\end{aligned}\quad (6.10)$$

where we have set, as it is customary,  $z \equiv e^{\beta\mu}$  and the *mean thermal wavelength* of the particle has been introduced: namely,

$$\lambda_T \equiv \frac{h}{\sqrt{2\pi m k T}} . \quad (6.11)$$

In addition, the *Bose-Einstein functions of order  $s$*  are defined to be

$$\begin{aligned}g_s(z) &:= \frac{1}{\Gamma(s)} \int_0^\infty dx \frac{x^{s-1}}{e^x z^{-1} - 1} \equiv \sum_{j=1}^\infty z^j j^{-s} , \\ \Re s &> 0, \quad 0 \leq z < 1 ; \\ \Re s &> 1, \quad z = 1 .\end{aligned}\quad (6.12)$$

Then we can write

$$\beta \lambda_T^D p = (2\mathbf{S} + 1) \{ -\lambda_T^D V_D^{-1} \ln(1 - z) + g_{(D+1)/2}(z) \} , \quad 0 \leq z < 1 . \quad (6.13)$$

In the very same way, we can also get

$$n = \frac{N}{V} = \frac{z(2\mathbf{S} + 1)}{V_D(1 - z)} + (2\mathbf{S} + 1) \lambda_T^{-D} g_{D/2}(z) . \quad (6.14)$$

To sum up, we can write the parametric state equation in the very simple form

$$\beta p = (2\mathbf{S} + 1) \{ -V_D^{-1} \ln(1 - z) + \lambda_T^{-D} g_{(D+1)/2}(z) \} ; \quad (6.15)$$

$$n = (2\mathbf{S} + 1) \left\{ \frac{z}{V_D(1 - z)} + \lambda_T^{-D} g_{D/2}(z) \right\} , \quad (6.16)$$

$$0 \leq z < 1 .$$



Let us now consider the distribution of the particles among the whole set of the excited states. According to eq. (6.12) we definitely find

$$\lim_{z \uparrow 1} g_{D/2}(z) = \begin{cases} \zeta(3/2), & \text{if } D = 3; \\ \infty, & \text{if } D = 1, 2. \end{cases} \quad (6.17)$$

This means that the Bose–Einstein condensation for free particles can occur in three spatial dimensions but *does not take place in the one- and two-dimensional cases*. After setting  $D = 3$  we can take the *thermodynamic limit*  $N \rightarrow \infty$ ,  $V \rightarrow \infty$ ,  $n = \text{constant}$ , so that we can eventually set

$$\begin{aligned} \lim_{z \uparrow 1} \lim_{V \rightarrow \infty} \frac{z(2S+1)}{V(1-z)} &:= n_0 < \infty; \\ \lim_{z \uparrow 1} \lim_{V \rightarrow \infty} V^{-1} \ln(1-z) &= 0. \end{aligned} \quad (6.18)$$

It is worth while to remark that, actually, the thermodynamic limit fully endorses the continuum limit. For a given particle density  $n$ , the *critical temperature* below which a non-vanishing finite density of molecules in the single-particle ground state does appear is clearly given by eq. (6.16): namely,

$$n = (2S+1) \lambda_T^{-3} \zeta(3/2) \quad \Leftrightarrow \quad T_c = \frac{2\pi\hbar}{mk} [n/(2S+1)\zeta(3/2)]^{2/3}. \quad (6.19)$$

Conversely, for a given equilibrium temperature  $T$ , the *critical particle density*, above which a non-vanishing finite density of molecules in the single-particle ground state does appear, is provided by

$$n_c = (2S+1) (2\pi mkT)^{3/2} \zeta(3/2)/h^3. \quad (6.20)$$

In summary, once the thermodynamic limit has been performed, we can write the state equation for the ideal boson gas of free particles in  $D = 3$  spatial dimensions in the splitted form

$$p = (2S+1) kT \lambda_T^{-3} g_{5/2}(z), \quad (6.21a)$$

$$n = (2\mathbf{S} + 1)\lambda_T^{-3} g_{3/2}(z) ; \quad (6.21b)$$

$$0 \leq z < 1 , \quad T \geq T_c ;$$

$$p = (2\mathbf{S} + 1)kT \lambda_T^{-3} \zeta(5/2) , \quad (6.22a)$$

$$n = n_0 + n_c = n_0 + (2\mathbf{S} + 1)\lambda_T^{-3} \zeta(3/2) ; \quad (6.22b)$$

$$z = 1 , \quad T \leq T_c , \quad n \geq n_c .$$

Also in the present case, according to eq. (4.9), we can define the order parameter for a given particle density  $n$ : namely,

$$\phi(T, v; \mathbf{S}) =: \frac{N_0}{N} = 1 - (2\mathbf{S} + 1) \frac{v}{\lambda_T^3} \zeta(3/2) = 1 - \left(\frac{T}{T_c}\right)^{3/2} \quad (6.23)$$

in which  $v := n^{-1}$  is the specific volume of the ideal system in the thermodynamic limit. Of course, we should write more properly

$$\phi(T, v; \mathbf{S}) = \begin{cases} 0 , & \text{iff } T \geq T_c ; \\ 1 - (T/T_c)^{3/2} , & \text{iff } T \leq T_c . \end{cases} \quad (6.24)$$

Now some remarks are in order. The first observation is that in the three dimensional case the Bose–Einstein condensation actually occurs and the molecules do accumulate in the single–particle ground state  $\mathbf{p} = 0$  : this means that *the condensation takes place in the momentum space* , the ideal system still keeping homogeneous in the configuration space. This is the main difference with respect to the harmonic traps condensation, in which the condensate wave function in configuration space is strongly peaked – see eq.s (5.3) and (5.4). The occurrence or not of the Bose–Einstein condensation is related to the boundedness or not of the particle density distribution among the single–particles excited states. This is why Bose–Einstein condensation does not appear for an ideal system of free particles in  $D = 1, 2$  , since we have in the thermodynamic limit

$$n_e(z) = - \lambda_T^{-2} \ln(1 - z) , \quad D = 2 ; \quad (6.25)$$

$$n_e(z) = \lambda_T^{-1} \sum_{j=1}^{\infty} z^j / \sqrt{j}, \quad D = 1 \quad (6.26)$$

and both the above expressions diverge when  $z \rightarrow 1$ . Turning back to the three dimensional case, the thermodynamic functions can be easily obtained from the granpotential *per* unit volume in the thermodynamic limit that reads – see eq.s (6.10), (6.21a) and (6.22a)

$$\lim_{V \rightarrow \infty} V^{-1} \Omega(z, T, V; \mathbf{S}) := \omega(z, T; \mathbf{S}) = (2\mathbf{S} + 1) kT \lambda_T^{-3} g_{5/2}(z) \quad (6.27)$$

which holds true in the whole range  $0 \leq z \leq 1$ . Then we can readily obtain the entropy, the internal energy and the heat capacity *per* unit volume: respectively,

$$s(z, T; \mathbf{S}) := \left( \frac{\partial \omega}{\partial T} \right)_{\mu} = \frac{5}{2} (2\mathbf{S} + 1) k \lambda_T^{-3} g_{5/2}(z) - nk \ln z, \quad (6.28)$$

$$u(z, T; \mathbf{S}) := n\mu - \frac{\partial}{\partial \beta} [\beta \omega(z, T; \mathbf{S})] = \frac{3}{2} (2\mathbf{S} + 1) kT \lambda_T^{-3} g_{5/2}(z), \quad (6.29)$$

$$c_v(z, T; \mathbf{S}) := T \left( \frac{\partial s}{\partial T} \right)_v = \frac{15}{4} (2\mathbf{S} + 1) k \frac{v}{\lambda_T^3} g_{5/2}(z) - \frac{9}{4} k \frac{g_{3/2}(z)}{g_{1/2}(z)}. \quad (6.30)$$

It is important to gather that all the above quantities goes to zero in the limits  $z \rightarrow 1$  and then  $T \rightarrow 0$ . This means that the Bose–Einstein condensate of free particles with vanishing momentum, which is the only surviving phase at extremely low temperatures, does not carry neither entropy, nor energy and nor even heat capacity. All those quantities are completely carried on by the normal phase, *i.e.* the Bose–Einstein vapour.

#### Appendix F: some special values of the Riemann's $\zeta$ -function

$$\zeta(1/2) = \zeta(1) = \infty;$$

$$\zeta(3/2) \simeq 2.612; \quad \zeta(2) = \frac{\pi^2}{6} \simeq 1.645; \quad \zeta(5/2) \simeq 1.341;$$

$$\zeta(3) \simeq 1.202; \quad \zeta(7/2) \simeq 1.127; \quad \zeta(4) = \frac{\pi^4}{90} \simeq 1.082.$$

### IX.7. Elementary excitations in liquid helium and superfluidity.

*The  $\lambda$ -transition.* As already noticed, it was F. London in 1938 the first one who suggested that the momentum space Bose–Einstein condensation is responsible for the superfluidity property of liquid  ${}^4\text{He}$ . As a matter of fact, helium is the only known substance that resists solidification under atmospheric pressure down to the lowest reachable temperatures. To solidify it requires an external pressure of at least 25 atm. This means that the only stable boson quantum liquid we have at very low temperatures is  ${}^4\text{He}$ , which consists of very weakly interacting atoms with integer total angular momenta. At a temperature  $T_\lambda = 2.18\text{ }^\circ\text{K}$  and for a particle density of  $2.16 \times 10^{22}\text{ atoms cm}^{-3}$  or, equivalently, for a specific volume of  $46.2 \times 10^{-24}\text{ cm}^3/\text{atom}$ ,  ${}^4\text{He}$  exhibits the remarkable so called  $\lambda$ -transition, at which the specific heat along the liquid–vapour equilibrium curve becomes logarithmically divergent according to the law

$$c_v \stackrel{T \simeq T_\lambda}{\sim} c \ln(k|T - T_\lambda|/q) + \begin{cases} c_\uparrow, & \text{if } T > T_\lambda \\ c_\downarrow, & \text{if } T < T_\lambda \end{cases} \quad (7.1)$$

where  $c, q, c_\uparrow, c_\downarrow$  are constants. The cusp-like shape of the specific heat curve near  $T_\lambda$  gives rise to the name  $\lambda$ -transition.

Above  $T_\lambda$ , liquid helium behaves like any other liquid and is called liquid helium I (He I). Below  $T_\lambda$ , liquid helium does exhibit the spectacular property of superfluidity, *i.e.* it is able to flow without viscosity or dissipation through the tiniest cracks: in this state it is called liquid helium II (He II). As a matter of fact, soon after Kamerlingh Omnes first liquified helium in 1908, it was found that He II crawls up the walls and coats all the internal surfaces of its container. More over, if placed in an open beaker, He II crawls up the walls, crosses the rim and flows out of the beaker: it clearly exhibits *super fluidity*.

It is significant that  ${}^4\text{He}$  does exhibit the  $\lambda$ -transition but  ${}^3\text{He}$  does not. Apart from

the difference in the atomic masses, the only difference between these two isotopes is that  $^4\text{He}$  are bosons whereas  $^3\text{He}$  are fermions.

*Hence it becomes rather natural to assume that the  $\lambda$ -transition just corresponds to a momentum space Bose–Einstein condensation modified by a weak atomic interaction.*

In fact, according to eq. (6.19), an ideal boson gas of particles with the same mass and specific volume as liquid  $^4\text{He}$  would undergo the Bose–Einstein condensation at  $T_c = 3.14$  °K, which is of the same order of magnitude as  $T_\lambda$ . Moreover, the angle-like shape of the specific heat curve (6.30) near  $T_c$  might be understood as the non-interacting counterpart of the corresponding cusp-like shaped  $\lambda$ -transition curve.

*The quasi-particles energy spectrum.* In order to support the above conjecture it becomes necessary to investigate the energy spectrum of He II. Lev Davidovic Landau (1941) *J. Phys. USSR* **5**, 71, was the first one who developed a simple theoretical scheme which explains reasonably well the behaviour of He II at temperatures below and not too close to the  $\lambda$ -transition. According to this scheme, the energy spectrum of the He II quantum liquid is depicted, *mutatis mutandis*, just like the phonon spectrum of the crystal lattice: the collective motions inside the quantum liquid can be treated as an assembly of non-interacting normal modes, the quanta of which are called *quasi-particles*. In other words, the liquid helium is treated as a weakly excited quantum mechanical system, in which deviations from the ground state, *i.e.* the superfluid corresponding to the Bose–Einstein condensate, are described in terms of an ideal gas of elementary excitations corresponding to the normal modes of He II, *i.e.* to the normal fluid.

At very low temperatures  $T \approx 0$  °K, there are no excitations at all and the whole fluid constitutes the Bose–Einstein weakly interacting condensate, which represents the superfluid non-degenerate ground state. In what follows, we assume that the superfluid

has vanishing drift velocity or, equivalently, we choose a reference frame in which the the superfluid mass is at rest, according to the picture of a Bose–Einstein condensate in momentum space build up of particles at rest,  $\mathbf{p} = 0$ . At higher temperatures, the *quasi*-particles of the liquid helium do appear, which constitute the normal fluid and coexist in thermal equilibrium with the superfluid condensate until, above  $T_\lambda$ , the Bose–Einstein condensate disappears and the whole quantum liquid behaves as a normal fluid He I.

Guided by purely empirical and phenomenological considerations, Landau proposed a dispersion relation for the energy and momentum of the *quasi*-particles, that means for the angular frequency and the wave number of the normal modes and, later on, a number of experimentalists investigated the spectrum of excitations in liquid helium II by measuring the scattering of long wavelength neutrons, the de Broglie wavelengths of which  $\ell = \hbar/p$  were ranging from 0.37 to 3.84 Å [ J.L. Yarnell *et al.* (1959) *Phys. Rev.* **113**, 1379, *ibid.* 1386; D.G. Henshaw & A.D.B. Woods (1961) *Phys. Rev.* **121**, 1266 ]. If the temperature is sufficiently low, between 1 and 2 °K, the scattering takes place mainly through the creation of elementary excitations, the energy and momentum of which are equal to the energy and momentum the neutrons transfer to the liquid. The results of those experimental investigations did exhibit a striking resemblance to the empirical dispersion relation suggested by Landau.

The most important features of the *quasi*-particle spectrum, which was obtained at temperatures ranging from 1 to 2 °K, are the following:

- (i) the best fit around  $p/\hbar = 0.55 \text{ \AA}^{-1}$  leads to the phonon–like dispersion law  $\hbar\omega = \varepsilon(p) = c_s p$  with a phonon velocity  $c_s = 239 \pm 5 \text{ m s}^{-1}$ , which is in excellent agreement with the measured value of the sound velocity in the liquid helium II;
- (ii) the *quasi*-particle spectrum passes through the local maximum value  $\varepsilon/k = 13.92 \pm$

0.10 °K at the wave number  $p/\hbar = 1.11 \pm 0.02 \text{ \AA}^{-1}$ ;

- (iii) the above local maximum is then followed by the local minimum at the wave number  $p/\hbar = 1.92 \pm 0.01 \text{ \AA}^{-1}$ , around which the dispersion law takes the form of the so called *Landau's roton spectrum*: namely,

$$\varepsilon(p) = \Delta + (p - p_0)^2/2\mu ; \quad (7.2)$$

$$\Delta/k = 8.65 \pm 0.04 \text{ °K} , \quad (7.3)$$

$$p_0/\hbar = 1.92 \pm 0.01 \text{ \AA}^{-1} , \quad (7.4)$$

$$\mu = 0.16 \pm 0.01 m_{\text{He}} ; \quad (7.5)$$

- (iv) above the wave number  $p/\hbar = 2.18 \text{ \AA}^{-1}$  the spectrum rises linearly with a slope still equal to  $c_s = 239 \pm 5 \text{ m s}^{-1}$ .

*Thermal equilibrium properties.* At very low temperatures, the average number of the quanta of the collective excitations, that means the average number of the *quasi*-particles, is very small, so that the particle interaction can be neglected and we can understand the collective density excitations of liquid helium II in terms of independent normal modes, the quanta of which are longitudinal phonons, according to our previous item (i). Since the  $^4\text{He}$  atoms are bosons, the *quasi*-particles in this system are bosons in turn. None the less, it is worth while to emphasize once again that the *quasi*-particles are *collective density excitations*, which represent rather different dynamic degrees of freedom in respect to those ones of individual helium atoms.

According to the Bose–Einstein condensation picture, we shall associate the superfluid component of He II, the only one that survives as  $T \rightarrow 0$ , to a weakly interacting Bose–Einstein condensate of energy  $U_0$ , whereas the normal fluid component of He II will be

constituted by an ideal gas of elementary excitations, the long wavelength phonon and roton *quasi*-particles, which account for the large scale density variations of the liquid matter. In analogy with eq.s (2.2), (2.3) for phonons and eq.s (3.31), (3.32) for photons, the average number of *quasi*-particles, the Helmholtz free energy and the internal energy at the equilibrium temperature  $T$  will be given by

$$N_{\text{q.p.}} = \frac{V}{(2\pi\hbar)^3} \int d^3p [\exp\{\beta\varepsilon(p)\} - 1]^{-1}, \quad (7.6)$$

$$F = U_0 + \frac{kTV}{(2\pi\hbar)^3} \int d^3p \ln[1 - \exp\{-\beta\varepsilon(p)\}], \quad (7.7)$$

$$U = U_0 + \frac{V}{(2\pi\hbar)^3} \int d^3p \frac{\varepsilon(p)}{\exp\{\beta\varepsilon(p)\} - 1}. \quad (7.8)$$

Notice that, if we indicate with  $N$  the mean total number of helium atoms, the average number of particles belonging to the Bose-Einstein condensate at the equilibrium temperature  $T \ll T_\lambda$  is given by  $N_0(T) = N - N_{\text{q.p.}}(T)$ . The entropy and the heat capacity at constant volume, which are solely carried on by the *quasi*-particle excitations, can be obtained from the basic thermodynamic formulae, viz.

$$S = - \left( \frac{\partial F}{\partial T} \right)_V; \quad C_V = \left( \frac{\partial U}{\partial T} \right)_V. \quad (7.9)$$

At very low temperatures, up to 0.5 °K, the thermodynamic behaviour of the quantum liquid is governed by the low lying excitations, namely by phonons with  $\varepsilon(p) = c_s p$ . Then we obtain

$$\begin{aligned} N_p &= \frac{4\pi V}{(2\pi\hbar)^3} \int_0^\infty dp p^2 [\exp\{\beta c_s p\} - 1]^{-1} \\ &= \frac{4\pi V (kT)^3}{(2\pi\hbar)^3 c_s^3} \int_0^\infty \frac{x^2 dx}{e^x - 1} = V \left( \frac{kT}{\hbar c_s} \right)^3 \frac{\zeta(3)}{\pi^2}, \end{aligned} \quad (7.10)$$

$$\begin{aligned} F_p &= kT \frac{4\pi V}{(2\pi\hbar)^3} \int_0^\infty dp p^2 \ln[1 - \exp\{-\beta c_s p\}] \\ &= -kT V \left( \frac{kT}{\hbar c_s} \right)^3 \frac{\pi^2}{90}, \end{aligned} \quad (7.11)$$

$$U_p = \frac{4\pi V}{(2\pi\hbar)^3} \int_0^\infty dp \frac{c_s p^3}{\exp\{\beta c_s p\} - 1} = kT V \left( \frac{kT}{\hbar c_s} \right)^3 \frac{\pi^2}{30}, \quad (7.12)$$



whence we immediately get the phonon heat capacity and entropy

$$C_p = kV \frac{2\pi^2}{15} \left( \frac{kT}{\hbar c_s} \right)^3 = 3S_p. \quad (7.13)$$

This very last equation shows explicitly that the particles belonging to the Bose–Einstein condensate, *i.e.* the superfluid component of He II, do not carry on neither entropy nor heat capacity, a quite remarkable property that will account for some peculiar behaviour of He II, as we shall see below.

At temperatures close to 0.5 °K, the second kind of *quasi*-particle excitations, namely the rotons with momenta in the vicinity of  $p_0$ , also shows up so that, between 0.5 °K and about 1.0 °K, the behaviour of He II is governed by phonons and rotons together. Above 1.0 °K, however, the phonon contributions to the various thermodynamic properties of the liquid becomes less and less important and the rotons are the only excitations that need to be considered. It is worth while to realize that, at all the temperatures of interest, that means  $T \sim 0.5 \div 1.5$  °K, the quantity  $\exp\{\beta\Delta\}$  is considerably larger than unity – see eq. (7.3). It follows therefrom from eq. (7.2) that we can safely approximate

$$[\exp\{\beta\varepsilon(p)\} - 1]^{-1} \approx \exp\{-\beta\Delta - (p - p_0)^2/2\mu kT\} \approx -\ln[1 - \exp\{-\beta\varepsilon(p)\}]. \quad (7.14)$$

Then, after setting  $p = p_0 + x\sqrt{2\mu kT}$ ,  $x_0 := p_0/\sqrt{2\mu kT} \gg 1$ , we obtain

$$\begin{aligned} N_r &= \frac{4\pi V}{(2\pi\hbar)^3} \int_0^\infty dp p^2 \exp\{-\beta\Delta - (p - p_0)^2/2\mu kT\} \\ &= \frac{4\pi V p_0^2}{(2\pi\hbar)^3} e^{-\beta\Delta} \sqrt{2\mu kT} \int_{-x_0}^\infty dx e^{-x^2} \left(1 + \frac{x}{x_0}\right)^2 \\ &\approx \frac{4\pi V p_0^2}{(2\pi\hbar)^3} e^{-\beta\Delta} \sqrt{2\mu kT} \int_{-\infty}^{+\infty} dx e^{-x^2} \\ &= \frac{V p_0^2}{2\pi^2 \hbar^3} e^{-\beta\Delta} \sqrt{2\pi\mu kT}. \end{aligned} \quad (7.15)$$

In a quite similar way we find

$$-\beta F_r \approx \frac{4\pi V}{(2\pi\hbar)^3} \int_0^\infty dp p^2 \exp\{-\beta\Delta - (p - p_0)^2/2\mu kT\} = N_r \quad (7.16)$$

$$U_r \approx -\frac{\partial}{\partial\beta} N_r = \left( \Delta + \frac{kT}{2} \right) N_r \quad (7.17)$$

and from the identity

$$\frac{\partial}{\partial T} N_r = \left( \frac{1}{2T} + \frac{\Delta}{k} \right) N_r \quad (7.18)$$

we immediately get the entropy and the heat capacity carried on by rotons

$$S_r \approx \frac{3}{2} k \left( 1 + \frac{2\Delta}{3kT} \right) N_r \quad (7.19)$$

$$C_r \approx \frac{3}{4} k \left( 1 + \frac{4\Delta}{3kT} + \frac{4\Delta^2}{3k^2T^2} \right) N_r \quad (7.20)$$

It is also worth while to remark that from eq. (7.13) it follows that the roton gas does satisfy the perfect gas state equation  $p_r V = N_r kT$ , whereas the state equation of the phonon gas can be read off eq.s (7.10) and (7.11): namely,

$$p_p V = \frac{\pi^4}{90\zeta(3)} N_p kT = \frac{\zeta(4)}{\zeta(3)} N_p kT \simeq 0.9 N_p kT . \quad (7.21)$$

When the temperature goes to zero the phonon pressure also vanishes with the fourth power of the temperature: this means that the Bose–Einstein condensate, *i.e.* the superfluid, is constituted by helium atoms carrying zero momenta, which do not produce any pressure on the container walls.

The total specific heat of the liquid helium II at constant volume is thereby given by the sum of the phonon and roton leading contributions: namely,

$$c_v \approx \frac{2k}{\varrho_{\text{He}}} \left\{ \frac{\pi^2}{15} \left( \frac{kT}{\hbar c_s} \right)^3 + \frac{(\Delta p_0)^2}{\hbar^3} e^{-\Delta/kT} (2\pi kT)^{-3/2} \right\} \quad (7.22)$$

where  $\varrho_{\text{He}} = V^{-1} M_{\text{He}} \simeq 0.14 \text{ g cm}^{-3}$  is the liquid helium density around the  $\lambda$ -point. The best fit of the above formula with the specific heat experimental data leads to a set of parameter values in very good agreement with those ones obtained by neutron scattering.

*Two fluids model and superfluidity criterion.* The unusual features of He II can be described in terms of a simple phenomenological model proposed by L. Tisza (1938) *Nature* **141**, 913 and known as the two fluids model. According to this model, the steady flowing He II, with a mass density  $\varrho$  and a drift velocity  $\mathbf{v}$ , is a mixture of a normal fluid, with mass density  $\varrho_n$  and drift velocity  $\mathbf{v}_n$ , and of a super fluid, with mass density  $\varrho_s$  and drift velocity  $\mathbf{v}_s$ , in such a way that we can write

$$\varrho = \varrho_n + \varrho_s; \quad \mathbf{v}\varrho = \mathbf{v}_n\varrho_n + \mathbf{v}_s\varrho_s. \quad (7.23)$$

The normal fluid is supposed to be a classical fluid, whereas the superfluid fulfills the two unusual properties:

- (i) it flows without viscosity and dissipation through a capillary of an extremely small diameter  $\sim 10^{-3} \div 10^{-2}$  cm;
- (ii) its entropy is zero: see eq. (7.13) and subsequent comments.

In accordance to the contents of the previous Sections, the super fluid is identified with the Bose–Einstein condensate and the normal fluid with the phonons and rotons ideal gas. The above two items are able to explain the most important effects displayed by He II.

*Mechanocaloric effect:* suppose that two containers  $A$  and  $B$  of He II are connected by a capillary and that  $p_A > p_B$ . Then superfluid flows from  $A$  to  $B$  until  $p_A = p_B$  but without entropy transfer. This means that the entropy *per* unit mass in  $A$  increases, whilst that of  $B$  decreases, so that  $A$  will warm up and  $B$  will cool down.

*Fountain effect:* it is the inverse mechanocaloric effect. Suppose we warm up  $A$  so that the entropy *per* unit mass of  $A$  increases by an amount  $\Delta s$ . If  $h(p, s) = M^{-1}H(p, S)$  denotes the specific enthalpy of the system and  $v$  its specific volume, then we have the equilibrium condition at a given temperature  $T$ : namely,

$$\Delta h = T\Delta s + v\Delta p = 0, \quad \Leftrightarrow \quad -\Delta p = \frac{T}{v} \Delta s \quad (7.24)$$

so that we have a pressure gradient towards  $A$  and a corresponding flow of superfluid through the capillary leak, until the differential of specific entropy will disappear.

*Second sound phenomenon:* the propagation of a sound wave in He II corresponds to a sinusoidal collective oscillation of  $\varrho_n$  and  $\varrho_s$  in phase one with each other, because only when both oscillate in phase the liquid total mass can undergo a sinusoidal collective motion. However, in a two fluids model, it is also possible to conceive a collective sinusoidal motion in which the normal and super fluid components do oscillate out of phase by  $\pi$ . When  $\varrho_n \simeq \varrho_s$ , this kind of collective motion can not be the propagation of a sound wave, for the total mass of the liquid is *grosso modo* at rest, namely  $\varrho \simeq \text{constant}$ . Instead, the latter kind of motion will represent a sinusoidal propagation of the entropy *per* unit mass, because the super fluid component does not carry entropy. As a consequence, we could produce this new kind of wave throughout the liquid by some local heating of He II. Then, the so established gradient of temperature will not propagate by diffusion, as for normal fluid convection, but shall propagate as a sinusoidal wave with a characteristic velocity  $c_{ss} \simeq c_s/\sqrt{3}$ , as predicted by Landau and confirmed by experiments at  $T \simeq 0.5$  °K. This is what is called the second sound phenomenon and is mainly due to phonons.

The relative amounts of normal fluid and super fluid components of He II can be measured by an ingenious experiment due to E.L. Andronikashvili (1946) *J. Phys. USSR* **10**, 201; (1948) *Zh. Experm. i Teor. Fiz.* **18**, 424. A pile of closely packed discs is rotated in a He II bath. The total moment of inertia of the system is measured as a function of the temperature within the range  $0.5 \div 1.0$  °K, when the liquid helium is in equilibrium with its own saturated vapour. The superfluid is not affected by rotation, owing to its lack of viscosity, but the normal fluid, which is constituted by phonons, rotons and any further excitations, is dragged around with the discs, leading to the measured value of the moment

of inertia, which turns out to be proportional to the ratio  $\varrho_n(T)/\varrho$ . The proportionality constant is determined by the fact that at the  $\lambda$ -transition point we have  $\varrho_n(T_\lambda)/\varrho = 1$ . The best fit of the experimental results is given by the law

$$\frac{\varrho_n(T)}{\varrho} = \begin{cases} (T/T_\lambda)^{5.6} & \text{if } T < T_\lambda ; \\ 1 & \text{if } T > T_\lambda . \end{cases} \quad (7.25)$$

Let us now deduce the *superfluidity criterion*. To this aim, it is convenient to consider two reference frames: namely, the laboratory reference frame  $K$ , in which the superfluid flows through a capillary with a drift velocity  $\mathbf{v}_s$ , and the superfluid rest frame  $K'$ , in which the capillary walls move with a drift velocity  $\mathbf{v}' = -\mathbf{v}_s$ . Let us first analyze the limiting case  $T \rightarrow 0$  in the superfluid rest frame  $K'$ . In this frame, the energy and total momentum of the superfluid are  $U_0$  and  $\mathbf{P}_0 = 0$  respectively, whereas the corresponding quantities for the moving capillary take the values  $E' = \frac{1}{2}M\mathbf{v}_s^2$  and  $\mathbf{P}' = -M\mathbf{v}_s$ , where  $M$  is the capillary mass.

In order that viscosity could appear, it is necessary that some fraction of normal fluid is created. This means that the capillary walls will transfer some amounts of momentum  $\Delta\mathbf{P}' = -M\Delta\mathbf{v}_s$  and energy  $\Delta E' = Mv_s\Delta v_s$  to the fluid, in such a way to create an elementary quantum excitation, *i.e.* a phonon of momentum  $p = M\Delta v_s \neq 0$  and of energy  $\varepsilon(p) = c_s p \leq \Delta E'$ , the missing energy being eventually dissipated into capillary walls heating. It follows therefrom that  $c_s \leq v_s$ , which means that, at  $T \rightarrow 0$ , some normal fluid cannot appear unless the capillary walls drift velocity is bigger than  $c_s$ .

From the point of view of a laboratory frame  $K$  observer, the above reasoning entails that viscosity and dissipation do not arise at  $T \rightarrow 0$ , as long as the superfluid flows with a drift velocity smaller than the sound velocity: this is the Landau's criterion for superfluidity. In the realistic case, when the temperature is low albeit finite, the critical velocity is defined to be  $v_c = \varepsilon(p)/p$  for a *quasi*-particle non-vanishing momentum transfer

$p = M\Delta v_s \neq 0$ . Then we have to take into account that phonons and rotons will be present and that *quasi*-particle scattering has also to be properly estimated within the energy-momentum balance. As a result, the critical velocity turns out to depend significantly upon the capillary geometry and to differ considerably from the sound velocity, the observed values ranging from about 0.1 cm/s to about 70 cm/s.

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## PROBLEMS

**Problem IX.1** Un cristallo unidimensionale é costituito da una catena lineare di  $N + 1$  atomi puntiformi identici di massa  $M$ , le cui posizioni di equilibrio corrispondono alle coordinate  $Z_n^{(0)} \equiv na$ ,  $n = 0, 1, \dots, N$ , dove  $a$  é il passo reticolare, in modo tale che la lunghezza a riposo della porzione di cristallo unidimensionale sia  $L = Na$ . Se indichiamo con  $Z_n$  la coordinata di Lagrange dello spostamento dalla posizione di equilibrio dell' $n$ -esimo atomo della catena, allora il potenziale interatomico si scrive

$$V(Z_0, \dots, Z_N) = \frac{1}{2} \sum_{n=0}^N \sum_{m=0}^N C_m (Z_n - Z_{n+m})^2, \quad C_m \geq 0,$$

dove abbiamo assunto che

$$Z_0(t) \equiv Z_N(t) \quad \Longleftrightarrow \quad Z_n(t) = Z_{n+N}(t), \quad \forall n = 0, 1, \dots, N.$$

Eliminiamo dalle soluzioni delle equazioni del moto del sistema quella corrispondente ad una traslazione della catena: imponiamo, cioé, che il baricentro della catena sia fisso

$$\sum_{n=1}^N Z_n(t) = 0.$$

- (i) Si mostri che la dinamica del cristallo unidimensionale é equivalente a quella di un insieme di  $N - 1$  oscillatori armonici unidimensionali reali e disaccoppiati, dotato di uno spettro discreto di frequenze con  $(N - 1)/2$  valori propri indipendenti, supponendo per semplicitá che  $N$  sia dispari.
- (ii) Nell'approssimazione di Debye, calcolare: l'energia libera di Helmholtz, l'entropia, l'energia interna e la capacitá termica a lunghezza costante del cristallo.
- (iii) Calcolare il numero medio di fononi presenti nel cristallo quando  $T \ll \Theta$ , dove  $\Theta$  é la temperatura di Debye.

*Solution.*

(i) Cerchiamo un sistema completo di modi elastici che soddisfino il requisito  $Z_n = Z_{n+N}$ , sulla base dei quali si possano sviluppare gli spostamenti dalla posizione di equilibrio degli atomi del cristallo unidimensionale. Introduciamo i vettori d'onda del cosiddetto reticolo inverso  $K_r \equiv 2\pi r/L$ ,  $r \in \mathbf{Z}$  e poniamo

$$U_n(K) \equiv \frac{1}{\sqrt{N}} \exp\{inaK\} = \frac{1}{\sqrt{N}} \exp\left\{2\pi i \frac{nr}{N}\right\}, \quad r \in \mathbf{Z},$$

in modo tale che

$$U_n(K) = U_{n+N}(K), \quad \forall n = 1, 2, \dots, N.$$

Avremo allora per  $r \neq r'$

$$\begin{aligned} \sum_{n=1}^N U_n(K) U_n^*(K') &= \frac{1}{N} \sum_{n=1}^N \exp\left\{2\pi i \frac{n}{N}(r - r')\right\} \\ &= \frac{1}{N} \exp\{2\pi i(r - r')/N\} \sum_{n=1}^N (\exp\{2\pi i(r - r')/N\})^{n-1} \\ &= \frac{1}{N} \exp\{2\pi i(r - r')/N\} \frac{\exp\{2\pi i(r - r')\} - 1}{\exp\{2\pi i(r - r')/N\} - 1} \\ &= 0, \quad r \neq r'. \end{aligned}$$

Di conseguenza risulta

$$\sum_{n=1}^N U_n(K) U_n^*(K') = \begin{cases} 1, & \text{se } r = r'; \\ 0, & \text{se } r \neq r'. \end{cases}$$

Osserviamo inoltre che si ha

$$U_n(K) = U_n(K \pm 2\pi/a), \quad \forall n = 1, 2, \dots, N.$$

Pertanto, supponendo  $N$  dispari e ponendo  $\nu = (N - 1)/2 \in \mathbf{N}$ , otteniamo che gli  $N$  vettori d'onda  $K_r = 2\pi r/L$ ,  $r = 0, \pm 1, \pm 2, \dots, \pm \nu$  costituiscono la zona di



Brillouin  $\mathcal{B}$  del cristallo lineare periodico. Si noti che i vettori d'onda  $\mathbf{K}$  della zona di Brillouin sono tali che  $|\mathbf{K}| \leq K_{\max}$  in cui

$$K_{\max} = \frac{\pi}{a} \left(1 - \frac{1}{N}\right) \simeq \frac{\pi}{a} .$$

I modi elastici

$$U_n(r) = \frac{1}{\sqrt{N}} \exp \left\{ 2\pi i \frac{nr}{N} \right\} \quad n = 1, 2, \dots, N \quad r = 0, \pm 1, \pm 2, \dots, \pm \nu$$

costituiscono un sistema ortonormale completo di movimenti del cristallo tali che

$$\begin{aligned} \sum_{n=1}^N U_n(r) U_n^*(s) &= \delta_{rs} , & r, s &= 0, \pm 1, \pm 2, \dots, \pm \nu , \\ \sum_{r=-\nu}^{+\nu} U_m(r) U_n^*(r) &= \delta_{mn} , & m, n &= 0, 1, 2, \dots, N . \end{aligned}$$

Poiché una qualunque funzione periodica  $f(n) = f(n + N)$  definita sul cristallo lineare può sempre essere sviluppata sulla base ortonormale e completa dei modi elastici  $U_n(r)$ , potremo scrivere

$$\begin{aligned} Z_n(t) &= \sum_{r=-\nu}^{+\nu} Q_r(t) U_n(r) \\ &= \frac{1}{\sqrt{N}} \sum_{r=-\nu}^{+\nu} Q_r(t) \exp \left\{ 2\pi i \frac{nr}{N} \right\} \\ &= \frac{Q_0(t)}{\sqrt{N}} + \frac{1}{\sqrt{N}} \sum_{K \in \mathcal{B}} Q_K(t) \exp \{ inaK \} . \end{aligned}$$

Poiché la funzione di Lagrange del cristallo lineare e periodico recita

$$L = \frac{M}{2} \sum_{n=0}^N \dot{Z}_n^2 - \frac{1}{2} \sum_{n=0}^N \sum_{m=0}^N C_m (Z_n - Z_{n+m})^2 ,$$

le equazioni di Eulero-Lagrange risultano

$$M\ddot{Z}_n + \sum_{m=0}^N C_m (2Z_n - Z_{n+m} - Z_{n-m}) = 0 .$$

Sviluppando sui modi elastici  $U_n(r)$  ricaviamo

$$\sum_{r=-\nu}^{+\nu} U_n(r) \left[ M\ddot{Q}_r + 4Q_r \sum_{m=0}^N C_m \sin^2(\pi mr/N) \right] = 0$$

e tenendo conto della completezza dei modi normali elastici otteniamo

$$\ddot{Q}_r + \omega_r^2 Q_r = 0 ,$$

ove

$$\omega_r^2 \equiv \frac{4}{M} \sum_{m=1}^N C_m \sin^2 \left( \frac{\pi mr}{N} \right) , \quad r = \pm 1, \pm 2, \dots, \pm \nu$$

sono le frequenze principali dei modi normali elastici del cristallo lineare con

$$\omega_r^2 = \omega_{-r}^2 , \quad \Leftrightarrow \quad \omega^2(K) = \omega^2(-K) ,$$

in cui

$$\omega^2(K) \equiv \frac{4}{M} \sum_{m=1}^N C_m \sin^2 \left( \frac{maK}{2} \right) , \quad K \in \mathcal{B} .$$

Dalla condizione che il baricentro sia fisso segue che dobbiamo escludere il modo nullo

$Q_0(t)$ : infatti,

$$\sum_{n=1}^N \exp \left\{ 2\pi i \frac{nr}{N} \right\} = 0 , \quad r \neq 0 .$$

Pertanto potremo scrivere in definitiva

$$Z_n(t) = \frac{1}{\sqrt{N}} \sum_{K \in \mathcal{B}} Q_K(t) \exp \{ inaK \} .$$

Il requisito che gli spostamenti degli atomi dalle posizioni di equilibrio siano quantità reali porta alla condizione di realtà

$$Q_K(t) = Q_{-K}^*(t) .$$

La soluzione piú generale delle equazioni di moto per le ampiezze dei modi normali elastici del cristallo periodico unidimensionale si scrive pertanto

$$\begin{aligned} Q_K(t) &= Q_-(K) \exp\{-i\omega(K)t\} + Q_+(K) \exp\{+i\omega(K)t\} \\ &= Q_-^*(-K) \exp\{+i\omega(-K)t\} + Q_+^*(-K) \exp\{-i\omega(-K)t\} \\ &= Q_-^*(-K) \exp\{+i\omega(K)t\} + Q_+^*(-K) \exp\{-i\omega(K)t\} \end{aligned}$$

ove

$$\omega(K) \equiv \sqrt{\frac{4}{M} \sum_{n=1}^N C_n \sin^2\left(\frac{naK}{2}\right)},$$

da cui si evincono le condizioni di realitá per le ampiezze  $Q_{\mp}(K)$  dei modi normali

$$Q_-(K) = Q_+^*(-K), \quad Q_+(K) = Q_-^*(-K).$$

In definitiva possiamo scrivere

$$Z_n(t) = \sum_{K \in \mathcal{B}} [Q_-(K) \exp\{-i\omega(K)t\} + Q_-^*(-K) \exp\{+i\omega(-K)t\}] \frac{\exp\{inaK\}}{\sqrt{N}}.$$

Tenendo conto del fatto che la zona di Brillouin é invariante per paritá rispetto ai vettori d'onda  $K$  e definendo  $Q_K \equiv Q_-(K)$  ne segue

$$Z_n(t) = \frac{1}{\sqrt{N}} \sum_{K \in \mathcal{B}} [Q_K \exp\{-i\omega(K)t + inaK\} + Q_K^* \exp\{i\omega(K)t - inaK\}].$$

Questa formula mostra che la dinamica del cristallo unidimensionale periodico con un numero dispari  $N$  di atomi puntiformi a baricentro fissato é equivalente a quella di un insieme di  $N - 1$  oscillatori armonici unidimensionali reali e disaccoppiati, dotato di uno spettro discreto di frequenze con  $(N - 1)/2$  valori propri indipendenti.

(ii) Per  $N \gg 1$  e ponendo  $\omega(K) = v|K|$ , dalla relazione

$$N \approx \frac{L}{2\pi} \int_{-2\pi\nu/a}^{+2\pi\nu/a} dK = \frac{L}{\pi v} \int_0^{k\Theta/\hbar} d\omega = \frac{k\Theta L}{\pi v\hbar},$$

segue l'energia libera nell'approssimazione di Debye

$$F_{\Theta}(T, L) = -kT \ln Z_{\Theta}(T, L) = U_0 + \frac{kTL}{\pi v} \int_0^{k\Theta/\hbar} d\omega \ln(1 - e^{-\beta\hbar\omega})$$

dove  $U_0 = Nk\Theta/2$  rappresenta la cosiddetta energia di punto zero del cristallo.

Dall'espressione per l'energia libera seguono quelle per l'entropia, l'energia interna e la capacità termica a lunghezza costante

$$F_{\Theta}(T, L) = U_0 + NkT \ln(1 - e^{-1/\xi}) - NkT\Delta(\xi) ,$$

$$S_{\Theta}(T, L) = 2Nk\Delta(\xi) - Nk \ln(1 - e^{-1/\xi}) ,$$

$$U(\xi) = U_0 + Nk\Theta \xi\Delta(\xi) ,$$

$$C_L(\xi) = Nk [\Delta(\xi) + \xi\Delta'(\xi)] ,$$

$$\Delta(\xi) \equiv \xi \int_0^{1/\xi} dx \frac{x}{e^x - 1} , \quad \xi \equiv (T/\Theta) .$$

Per quanto concerne la pressione, tenuto conto del fatto che  $L = Na$ , abbiamo

$$p \equiv - \left( \frac{\partial F_{\Theta}}{\partial L} \right)_T = - \frac{kT}{\pi v} \int_0^{k\Theta/\hbar} d\omega \ln(1 - e^{-\beta\hbar\omega}) = \frac{kT}{a} \left\{ \Delta(\xi) - \ln(1 - e^{-1/\xi}) \right\} .$$

Dagli andamenti della funzione di Debye del cristallo unidimensionale

$$\Delta(\xi) \underset{\xi \downarrow 0}{\sim} \frac{\pi^2}{6} \xi , \quad \lim_{\xi \rightarrow \infty} \Delta(\xi) = 1 ,$$

segue che

$$C_L(T) \overset{T \ll \Theta}{\sim} \frac{N\pi^2}{3\Theta} T , \quad C_L(T) \overset{T \gg \Theta}{\sim} Nk .$$

(iii) Nell'approssimazione di Debye, il numero medio dei fononi del cristallo lineare é

$$\langle N_{\text{fononi}} \rangle \approx \frac{L}{\pi v} \int_0^{k\Theta/\hbar} \frac{d\omega}{e^{\beta\hbar\omega} - 1} \overset{T \ll \Theta}{\sim} \frac{L}{\pi v} \int_0^{k\Theta/\hbar} d\omega e^{-\beta\hbar\omega} \approx N \frac{T}{\Theta} .$$

**Problem IX.2** Si consideri una porzione di solido cristallino con volume  $V$  costituita da un reticolo di  $N$  siti, al centro dei quali si trovano le molecole del cristallo formate da  $A$

atomi puntiformi. Si assuma valida l'approssimazione di Debye, in cui la densità dei modi normali di propagazione delle onde elastiche è data da

$$\varrho_D(\omega) = \frac{V}{2\pi^2} \omega^2 \left( \frac{2}{v_T^3} + \frac{1}{v_L^3} \right) \vartheta(\omega) \vartheta(\omega_{\max} - \omega) ,$$

dove  $v_T$  e  $v_L$  sono rispettivamente le velocità trasversa e longitudinale delle onde elastiche, mentre  $\omega_{\max}$  è la frequenza angolare massima e  $\vartheta$  indica la distribuzione a gradino di Heaviside. Si determini:

- (i) l'energia interna e la capacità termica a volume costante  $C_V$  ;
- (ii) la pressione e la capacità termica a pressione costante  $C_P$  ;
- (iii) l'equazione dell'adiabatica e il rapporto ( $C_P/C_V$ ) .

*Soluzione*

- (i) Dalla relazione

$$3AN = \frac{V}{2\pi^2} \left( \frac{1}{v_L^3} + \frac{2}{v_T^3} \right) \int_0^{k\Theta/\hbar} d\omega \omega^2 = \frac{V}{2\pi^2} \left( \frac{1}{v_L^3} + \frac{2}{v_T^3} \right) \frac{k^3 \Theta^3}{3\hbar^3}$$

segue l'energia libera nell'approssimazione di Debye

$$F_\Theta(T, V) = -kT \ln Z_\Theta(T, V) = U_0 + kT \frac{V}{2\pi^2} \left( \frac{1}{v_L^3} + \frac{2}{v_T^3} \right) \int_0^{k\Theta/\hbar} d\omega \omega^2 \ln(1 - e^{-\beta\hbar\omega}) .$$

dove  $U_0 = V_0 + (9/8)ANk\Theta$  rappresenta la cosiddetta energia di punto zero del cristallo. Dall'espressione per l'energia libera seguono quelle per l'entropia e l'energia

interna

$$\begin{aligned}
F_{\Theta}(T, V) - U_0 &= 3ANkT \ln \left( 1 - e^{-1/\xi} \right) - ANkT \Delta(\xi) , \\
&= -VkT \left( \frac{1}{v_L^3} + \frac{2}{v_T^3} \right) \frac{k^3 \Theta^3}{6\pi^2 \hbar^3} \left\{ \frac{1}{3} \Delta(\xi) - \ln \left( 1 - e^{-1/\xi} \right) \right\} , \\
S_{\Theta}(T, V) &= 3ANk \left\{ \frac{4}{3} \Delta(\xi) - \ln \left( 1 - e^{-1/\xi} \right) \right\} , \\
U(\xi) &= U_0 + 3ANk\Theta \xi \Delta(\xi) , \\
C_V(\xi) &= 3ANk \left[ \Delta(\xi) + \xi \Delta'(\xi) \right] \equiv 3ANk D(\xi) , \\
\Delta(\xi) &\equiv 3\xi^3 \int_0^{1/\xi} dx \frac{x^3}{e^x - 1} , \quad \xi \equiv (T/\Theta) .
\end{aligned}$$

(ii) La pressione risulta

$$p \equiv - \left( \frac{\partial F_{\Theta}}{\partial V} \right)_T = \left( \frac{1}{v_L^3} + \frac{2}{v_T^3} \right) \frac{k^4 \Theta^4}{6\pi^2 \hbar^3} \left\{ \frac{\xi}{3} \Delta(\xi) - \xi \ln \left( 1 - e^{-1/\xi} \right) \right\}$$

e l'equazione di stato nell'approssimazione di Debye diviene pertanto

$$pv = k\Theta \left\{ \frac{\xi}{3} \Delta(\xi) - \xi \ln \left( 1 - e^{-1/\xi} \right) \right\} ,$$

dove  $v \equiv V/3AN$  rappresenta al solito il volume per atomo. Dagli andamenti

$$\Delta(\xi) \stackrel{T \ll \Theta}{\approx} \frac{\pi^4}{5} \xi^3 , \quad \Delta(\xi) \stackrel{T \gg \Theta}{\approx} 1$$

seguono le espressioni approssimate dell'equazione di stato nei regimi di bassa e alta temperatura rispettivamente, vale a dire

$$pv \stackrel{T \ll \Theta}{\approx} kT \frac{\pi^4}{15} \left( \frac{T}{\Theta} \right)^3 , \quad pv \stackrel{T \gg \Theta}{\approx} kT \ln \left( \frac{T}{\Theta} \right) .$$

La capacità termica a pressione costante segue subito dalla definizione e dal fatto che l'entropia per atomo è una funzione della sola  $\xi$ : infatti,

$$\begin{aligned}
C_p &\equiv T \left( \frac{dS}{dT} \right)_p = T \frac{dS}{d\xi} \left( \frac{d\xi}{dT} \right)_p \\
&= 3ANk \left\{ \frac{4}{3} \xi \Delta'(\xi) + \frac{1/\xi}{e^{\xi} - 1} \right\} \\
&= 3ANk D(\xi) = C_V .
\end{aligned}$$

(iii) Poichè l'entropia per atomo del cristallo è funzione della sola  $\xi$ , segue subito che  $dS = 0 \Leftrightarrow \xi = \text{costante}$ . Pertanto le equazioni dell'adiabatica e dell'isoterma coincidono per il cristallo:  $PV = \text{costante}$ . Di conseguenza si ha  $\gamma = 1$ , come da sopra esplicitamente evidente.

**Problem IX.3** Si consideri un gas ideale di molecole monoatomiche di massa  $m$  soggette ad un potenziale esterno del tipo *trappola armonica isotropa* :

$$V(x, y, z) = \frac{m}{2}\omega^2 (x^2 + y^2 + z^2) .$$

Si supponga che il sistema si trovi all'equilibrio termico con un termostato a temperatura assoluta  $T$ . Si chiede di determinare:

- (i) la funzione di partizione di singola molecola nei casi classico e quantistico;
- (ii) perchè ed in quali condizioni può avvenire la condensazione di Bose-Einstein;
- (iii) una stima della temperatura critica.

*Soluzione*

(i) Funzione di Partizione Canonica di singola molecola:

$$Z_1^{(c)}(\xi) = \xi^{-3} , \quad \xi \equiv \frac{\hbar\omega}{kT} ;$$

$$Z_1^{(q)}(\xi) = \frac{1}{8} \operatorname{csch}^3(\xi/2) .$$

(ii) Gli autovalori dell'energia di singola molecola sono dati da

$$E_{n_x, n_y, n_z} = \hbar\omega(n_x + n_y + n_z) + \frac{3}{2}\hbar\omega ,$$

$$n_x + 1 \in \mathbf{N} , \quad n_y + 1 \in \mathbf{N} , \quad n_z + 1 \in \mathbf{N} ,$$

da cui si ottiene immediatamente il numero medio delle molecole per un gas ideale di

Bose-Einstein:

$$\langle N \rangle = \sum_{n_x=0}^{\infty} \sum_{n_y=0}^{\infty} \sum_{n_z=0}^{\infty} \frac{\exp\{\beta\mu - \beta\epsilon_0 - \beta\hbar\omega(n_x + n_y + n_z)\}}{1 - \exp\{\beta\mu - \beta\epsilon_0 - \beta\hbar\omega(n_x + n_y + n_z)\}}$$

$$= \frac{\exp\{\beta\mu - \beta\epsilon_0\}}{1 - \exp\{\beta\mu - \beta\epsilon_0\}} + \langle N_* \rangle , \quad \mu < \epsilon_0 ,$$

dove si é posto per brevità  $\epsilon_0 \equiv 3\hbar\omega/2$  mentre  $\langle N_* \rangle$  indica il numero medio delle molecole che occupano gli stati eccitati di singola molecola. Dal momento che  $\Delta E = \hbar\omega$ , per una intensità della trappola armonica sufficientemente debole lo spettro può considerarsi quasi continuo ed é lecito passare al limite del continuo sostituendo le sommatorie con integrali:

$$\sum_{n=0}^{\infty} \mapsto \int_0^{\infty} dn = \int_0^{\infty} \frac{dE}{\hbar\omega} .$$

Pertanto potremo scrivere

$$\begin{aligned} \langle N_* \rangle &\simeq \int_0^{\infty} dn_x \int_0^{\infty} dn_y \int_0^{\infty} dn_z \frac{\exp\{\beta\mu - \beta\epsilon_0 - \beta\hbar\omega(n_x + n_y + n_z)\}}{1 - \exp\{\beta\mu - \beta\epsilon_0 - \beta\hbar\omega(n_x + n_y + n_z)\}} \\ &= \sum_{j=0}^{\infty} \exp\{\beta(\mu - \epsilon_0)(j+1)\} \left[ \int_0^{\infty} dn \exp\{-\beta\hbar\omega n(j+1)\} \right]^3 \\ &= \sum_{j=1}^{\infty} \left( \frac{kT}{j\hbar\omega} \right)^3 \exp\{j\beta(\mu - \epsilon_0)\} = \left( \frac{kT}{\hbar\omega} \right)^3 g_3(z_*) , \end{aligned}$$

in cui si é posto

$$z_* \equiv \exp\{\beta(\mu - \epsilon_0)\} = z \exp\{-3\beta\hbar\omega/2\} ,$$

mentre con  $g_s(z)$  si indicano al solito le *funzioni di Bose-Einstein di ordine s*:

$$g_s(z) \equiv \sum_{j=1}^{\infty} \frac{z^j}{j^s} , \quad \Re s > 1 , \quad |z| \leq 1 .$$

In definitiva, nel limite del continuo potremo scrivere

$$\langle N \rangle \simeq \langle N_0 \rangle + \langle N_* \rangle = \frac{z_*}{1 - z_*} + \left( \frac{kT}{\hbar\omega} \right)^3 g_3(z_*) , \quad z_* < 1 ,$$

da cui il parametro d'ordine

$$\phi \equiv \frac{\langle N_0 \rangle}{\langle N \rangle} = 1 - \frac{(kT)^3 g_3(z_*)}{\langle N \rangle (\hbar\omega)^3} .$$



Ora, poiché la funzione  $g_3(z_*)$  è monotona crescente e superiormente limitata in quanto

$$\lim_{z_* \uparrow 1} g_3(z_*) = \zeta(3) ,$$

dove  $\zeta(s)$  è la *funzione  $\zeta$  di Riemann*, abbiamo che, nel limite del continuo, la condensazione di Bose-Einstein ha luogo per valori non nulli del parametro d'ordine  $\phi$ : vale a dire,

$$0 < \frac{(kT)^3 \zeta(3)}{\langle N \rangle (\hbar\omega)^3} < 1 .$$

(iii) Il limite termodinamico si ottiene riducendo l'intensità della trappola armonica in modo tale che

$$\langle N \rangle \rightarrow \infty , \quad \omega \rightarrow 0 , \quad \langle N \rangle \omega^3 \equiv \omega_*^3 = \text{costante} .$$

Nel limite termodinamico e nel limite del continuo la temperatura critica è pertanto data da

$$\phi = 0 \quad \Leftrightarrow \quad \frac{(kT_c)^3 \zeta(3)}{(\hbar\omega_*)^3} = 1 \quad \Leftrightarrow \quad kT_c = \frac{\hbar\omega_*}{\sqrt[3]{\zeta(3)}} .$$

**Problem IX.4** Si consideri un gas ideale di molecole monoatomiche di massa  $m$  soggette ad un potenziale esterno del tipo *trappola armonica* :

$$V(x, y, z) = \frac{m}{2} \omega^2 (x^2 + y^2 + z^2) .$$

Si supponga che il sistema si trovi all'equilibrio termico con un termostato a temperatura assoluta  $T$ . Si chiede di determinare:

- (i) l'equazione di stato e l'entropia, nel caso in cui il gas sia costituito di  $N$  molecole racchiuse in un recipiente sferico di raggio  $R$  e gli effetti quantistici siano trascurabili;
- (ii) l'equazione di stato in forma parametrica nel caso quantistico, supponendo completamente simmetrica la funzione d'onda del sistema e passando al limite  $R \rightarrow \infty$ ;

(iii) se il sistema può condensare.

*Soluzione*

(i) La funzione di partizione classica per gli oscillatori indipendenti é data da

$$\begin{aligned} Z_N^{(c)}(T, R; \omega) &= \frac{(2\pi mkT)^{3N/2}}{h^{3N}} \left[ 4\pi \int_0^R dr r^2 \exp \left\{ -\beta \frac{m}{2} \omega^2 r^2 \right\} \right]^N \\ &= 2^N \pi^{-N/2} \left( \frac{kT}{\hbar\omega} \right)^{3N} \left[ \gamma \left( \frac{3}{2}, \frac{m\omega^2 R^2}{2kT} \right) \right]^N . \end{aligned}$$

Pertanto la pressione radiale isotropa e l'equazione di stato si scrivono

$$\begin{aligned} p &= kT \frac{\partial}{\partial V} \ln Z_N^{(c)}(T, R; \omega) \\ &= \frac{kT}{4\pi R^2} \frac{\partial}{\partial R} \ln Z_N^{(c)}(T, R; \omega) \\ &= \frac{Nm\omega^2}{4\pi R} \frac{d}{du} \ln \gamma \left( \frac{3}{2}, u \right) \Big|_{u=m\beta\omega^2 R^2/2} \\ &= \frac{2NkT}{3V} \left[ u \frac{d}{du} \ln \gamma \left( \frac{3}{2}, u \right) \right]_{u=m\beta\omega^2 R^2/2} . \end{aligned}$$

L'entropia classica si ricava dalla formula

$$\begin{aligned} S^{(c)} &= k \left( 1 - \frac{\beta\partial}{\partial\beta} \right) \ln Z_N^{(c)}(T, R; \omega) \\ &= 4Nk - 3Nk \ln(\beta\hbar\omega) + kN \ln \left[ \frac{2\gamma(3/2, u)}{\sqrt{\pi}} \right]_{u=m\beta\omega^2 R^2/2} \\ &\quad - Nk \left[ u \frac{d}{du} \ln \gamma \left( \frac{3}{2}, u \right) \right]_{u=m\beta\omega^2 R^2/2} . \end{aligned}$$

(ii) Nel limite  $R \rightarrow \infty$  gli autovalori dell'energia di singola molecola sono dati da

$$\begin{aligned} E_{n_x, n_y, n_z} &= \hbar\omega(n_x + n_y + n_z) + \frac{3}{2}\hbar\omega , \\ n_x + 1 &\in \mathbf{N} , \quad n_y + 1 \in \mathbf{N} , \quad n_z + 1 \in \mathbf{N} , \end{aligned}$$

da cui si ottiene immediatamente l'equazione di stato in forma parametrica per un

gas ideale di Bose-Einstein:

$$\begin{aligned}\beta\Omega(\mu, \beta; g, \omega) &= - \sum_{n_x=0}^{\infty} \sum_{n_y=0}^{\infty} \sum_{n_z=0}^{\infty} \ln [1 - \exp \{\beta\mu - \beta\epsilon_0 - \beta\hbar\omega(n_x + n_y + n_z)\}] , \\ \langle N \rangle &= \sum_{n_x=0}^{\infty} \sum_{n_y=0}^{\infty} \sum_{n_z=0}^{\infty} \frac{\exp \{\beta\mu - \beta\epsilon_0 - \beta\hbar\omega(n_x + n_y + n_z)\}}{1 - \exp \{\beta\mu - \beta\epsilon_0 - \beta\hbar\omega(n_x + n_y + n_z)\}} \\ &= \frac{\exp \{\beta\mu - \beta\epsilon_0\}}{1 - \exp \{\beta\mu - \beta\epsilon_0\}} + \langle N_* \rangle , \quad \mu < \epsilon_0 ,\end{aligned}$$

dove si é posto per brevità  $\epsilon_0 \equiv 3\hbar\omega/2$  mentre  $\langle N_* \rangle$  indica il numero medio delle molecole che occupano gli stati eccitati di singola molecola. Dal momento che la separazione tra due livelli energetici successivi é pari a  $\Delta E = \hbar\omega$  avremo che lo spettro dell'energia si puó considerare come quasi continuo quando l'intensità della trappola armonica é molto debole, cioè  $\omega \downarrow 0$ . In questo caso é lecito passare al limite del continuo sostituendo le sommatorie con integrali:

$$\sum_{n=0}^{\infty} \longmapsto \int_0^{\infty} dn .$$

Pertanto potremo scrivere

$$\begin{aligned}\beta\Omega(\mu, \beta; g, \omega) &= \\ &= - \int_0^{\infty} dn_x \int_0^{\infty} dn_y \int_0^{\infty} dn_z \ln [1 - \exp \{\beta\mu - \beta\epsilon_0 - \beta\hbar\omega(n_x + n_y + n_z)\}] .\end{aligned}$$

Supponendo  $\exp \{\beta(\mu - \epsilon_0)\} \leq 1$  potremo sviluppare in serie il logaritmo naturale

$$\begin{aligned}\beta\Omega(\mu, \beta; g, \omega) &= \sum_{j=1}^{\infty} \frac{1}{j} \exp \{j\beta\mu - j\beta\epsilon_0\} \\ &\times \int_0^{\infty} dn_x \int_0^{\infty} dn_y \int_0^{\infty} dn_z \exp \{-j\beta\hbar\omega(n_x + n_y + n_z)\} \\ &= \left(\frac{kT}{\hbar\omega}\right)^3 \sum_{j=1}^{\infty} \frac{1}{j^4} \exp \{j\beta\mu - j\beta\epsilon_0\} \\ &= \left(\frac{kT}{\hbar\omega}\right)^3 g_4(\exp \{\beta\mu - \beta\epsilon_0\}) ,\end{aligned}$$

dove con  $g_s(z)$  si indicano al solito le *funzioni di Bose-Einstein di ordine s*:

$$g_s(z) \equiv \sum_{j=1}^{\infty} \frac{z^j}{j^s}, \quad \Re s > 1, \quad 0 \leq z \leq 1.$$

Si noti che l'ultima espressione per il granpotenziale ha validit   $\forall \mu \in \mathbf{R}$  e rappresenta pertanto la continuazione analitica dello sviluppo in serie sopra impiegato. In modo del tutto analogo per il numero medio di molecole otteniamo

$$\begin{aligned} \langle N_* \rangle &\simeq \int_0^{\infty} dn_x \int_0^{\infty} dn_y \int_0^{\infty} dn_z \frac{\exp\{\beta\mu - \beta\epsilon_0 - \beta\hbar\omega(n_x + n_y + n_z)\}}{1 - \exp\{\beta\mu - \beta\epsilon_0 - \beta\hbar\omega(n_x + n_y + n_z)\}} \\ &= \sum_{j=0}^{\infty} \exp\{\beta(\mu - \epsilon_0)(j+1)\} \left[ \int_0^{\infty} dn \exp\{-\beta\hbar\omega n(j+1)\} \right]^3 \\ &= \sum_{j=1}^{\infty} \left( \frac{kT}{j\hbar\omega} \right)^3 \exp\{j\beta(\mu - \epsilon_0)\} = \left( \frac{kT}{\hbar\omega} \right)^3 g_3(z_*), \end{aligned}$$

in cui si   posto

$$z_* \equiv \exp\{\beta(\mu - \epsilon_0)\} = z \exp\{-3\beta\hbar\omega/2\},$$

In definitiva, nel limite del continuo potremo scrivere

$$\begin{aligned} \Omega &= - \frac{(kT)^4}{(\hbar\omega)^3} g_4(z_*), \\ \langle N \rangle &= \langle N_0 \rangle + \langle N_* \rangle \\ &= \frac{z_*}{1 - z_*} + \left( \frac{kT}{\hbar\omega} \right)^3 g_3(z_*), \quad z_* < 1, \end{aligned}$$

da cui il parametro d'ordine

$$\phi \equiv \frac{\langle N_0 \rangle}{\langle N \rangle} = 1 - \frac{(kT)^3 g_3(z_*)}{\langle N \rangle (\hbar\omega)^3}.$$

(iii) Poich  la funzione  $g_3(z_*)$    monotona crescente e superiormente limitata in quanto

$$\lim_{z_* \uparrow 1} g_3(z_*) = \zeta(3),$$

dove  $\zeta(s)$  é la *funzione  $\zeta$  di Riemann*, abbiamo che, nel limite del continuo, la condensazione di Bose-Einstein ha luogo per valori non nulli del parametro d'ordine  $\phi$ : vale a dire,

$$0 < \frac{(kT)^3 \zeta(3)}{\langle N \rangle (\hbar\omega)^3} < 1 .$$

Il limite termodinamico si ottiene riducendo l'intensitá della trappola armonica in modo tale che

$$\langle N \rangle \rightarrow \infty , \quad \omega \rightarrow 0 , \quad \langle N \rangle \omega^3 \equiv \omega_*^3 = \text{costante} .$$

Nel limite termodinamico e nel limite del continuo la temperatura critica é pertanto data da

$$\phi = 0 \quad \Leftrightarrow \quad \frac{(kT_c)^3 \zeta(3)}{(\hbar\omega_*)^3} = 1 \quad \Leftrightarrow \quad kT_c = \frac{\hbar\omega_*}{\sqrt[3]{\zeta(3)}} .$$