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1977 J. Phys. A: Math. Gen. 10 561

(http://iopscience.iop.org/0305-4470/10/4/018)

J. Phys. A: Math. Gen., Vol. 10, No. 4, 1977. Printed in Great Britain. © 1977

Criteria for the onset of Bose–Einstein condensation in ideal systems confined to restricted geometries†

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Received 20 September 1976, in final form 6 December 1976

Abstract. Several authors have proposed criteria for the onset of Bose–Einstein condensation in finite systems. Using mathematical techniques developed by Pathria and collaborators, we have systematically examined these various proposals by applying them to an ideal Bose gas confined to a cuboidal enclosure under periodic boundary conditions. The 'transition points' thus obtained have been subjected to a comparative study, which indicates that the most useful general criterion is the macroscopic one based on the maximum of the specific heat C_V.

1. Introduction

In an infinite system the onset of Bose–Einstein condensation takes place abruptly at a well defined temperature $T_0(\infty)$. In finite systems, however, the corresponding transition is spread over a finite range of temperatures, ΔT, around $T_0(\infty)$; in several cases, $\Delta T/T_0(\infty) = O(\bar{l}/L_<)$ where $\bar{l}\,[=(V/N)^{1/3}]$ is the mean interparticle distance while $L_<$ is the length of the shortest side of the container. Nevertheless, comparison with the experimental situation in superfluid ^{4}He suggests that some sort of a 'transition temperature' should be defined for finite systems as well (see Eggington 1975). This leads to a variety of criteria to mark the 'onset' of Bose–Einstein condensation in such systems. These criteria, in general, lead to different 'transition temperatures' in the range ΔT; of course, in the thermodynamic limit, they all coalesce to the bulk value $T_0(\infty)$.

Whereas several authors have suggested criteria for the onset of Bose–Einstein condensation in finite systems, no systematic examination and comparison of these seems to have been done so far. The importance of making such a study is twofold. Firstly, one would like to know which, of the many criteria put forward, are really promising and which, if any, should be discarded. Secondly, one may be able to establish an ordering of these criteria on the basis of the transition points they give for the onset of Bose–Einstein condensation. The results of a theoretical investigation of these questions, as applied to a gas of non-interacting bosons, are being reported in this paper.

To analyse a finite Bose–Einstein system by rigorous analytic means one must somehow evaluate the summations-over-states which appear in the various expressions pertaining to the system. In the bulk case one resorts to the customary procedure of converting these summations into integrations. For a finite system, however, such a

† Work supported in part by the National Research Council of Canada.

procedure can introduce serious inaccuracies, so one must handle the summations-over-states rather directly. This can be done by employing the mathematical techniques developed recently by Pathria (1972a), by Greenspoon and Pathria (1974) and by Chaba and Pathria (1975, 1976).

Using the grand canonical ensemble we first of all study the rigorous, asymptotic behaviour of the various thermodynamic and statistical quantities pertaining to an ideal Bose gas confined to an arbitrary, finite, cuboidal enclosure under periodic boundary conditions; in particular, we consider the thin-film, the square-channel and the cubic geometries. Making use of these results we then examine the criteria proposed by various authors for the onset of Bose–Einstein condensation in a finite system. For instance, Goble and Trainor (1966) have suggested the use of certain ground-state, and excited-states, properties of the system. Greenspoon and Pathria (1973, 1974) have introduced the thermogeometric parameters $y_j(T)$, $j = 1, 2, 3$, and have observed that $y_j = \pi(-\mu/\Delta_j)^{1/2}$ where μ is the chemical potential of the system and Δ_j $(= \hbar^2/ML_j^2)$ is a measure of the discreteness of its energy levels. The parameters y_j^2, therefore, represent a 'reduced' chemical potential of the system. The term 'thermogeometric' reflects the dual nature of these parameters, in that they are related to the thermodynamical parameter μ as well as to the geometric parameters Δ_j. Subsequently it was shown (Greenspoon and Pathria 1975) that the thermogeometric parameters $y_j(T)$ are more directly related to the (scaled) correlation length ξ in the system. This suggested considering certain properties of $y_j(T)$ and $y_j^{-1}(T)$ as other possible criteria. Now, thermodynamic quantities, such as the specific heat C_V, have been used previously by Goble and Trainor (1966) and by Greenspoon and Pathria (1974). Moreover, London (1938), Osborne (1949), Ziman (1953) and Krueger (1968) have also proposed certain criteria, the details of which need not be discussed at this point. We have scrutinized all these criteria to determine their relative merits and demerits. In addition, we have made some observations on the relative ordering of the various criteria investigated.

Three basic types of criteria appear in this study: (i) macroscopic ones; (ii) microscopic ones; and (iii) hybrid ones. Criteria based on the ground-state properties of the system are regarded to be of type (iii) because, when we are dealing with the condensate, we are considering a microscopic state with a macroscopic occupation number; hence, the use of the word 'hybrid' in describing criteria of this type.

2. Formulation of the problem

We consider a Bose–Einstein system of N non-interacting particles confined to a finite, cuboidal geometry $(L_1 \times L_2 \times L_3)$ with the single-particle energy levels ϵ_i. The mean occupation numbers $\langle n_i \rangle$, in the grand canonical ensemble, are given by

$$\langle n_i \rangle = (e^{\alpha + \epsilon_i/kT} - 1)^{-1}, \tag{1}$$

with

$$\alpha = -\mu/kT, \tag{2}$$

μ being the chemical potential of the system. As shown by Pathria (1972a), the thermodynamic properties of the system can be expressed in terms of the functions

$$Z_s = \sum_i (\epsilon_i/kT)^s \langle n_i \rangle \qquad (s = 0, 1, 2, \ldots), \tag{3}$$

$$G_s = \sum_i (\epsilon_i/kT)^s(\langle n_i\rangle + \langle n_i\rangle^2) = -(\partial Z_s/\partial\alpha)_{T,L_j}, \tag{4}$$

$$G_s' = -(\partial G_s/\partial\alpha)_{T,L_j}, \qquad G_s'' = -(\partial G_s'/\partial\alpha)_{T,L_j}, \qquad \text{etc.} \tag{5}$$

For instance, the specific heat at constant volume, C_V, is given by

$$C_V = k(G_2 - G_1^2/G_0). \tag{6}$$

Equation (6) and corresponding formulae for other thermodynamic quantities hold irrespective of the dimensionality of the system, the shape and size of the enclosure, and the type of boundary conditions imposed on the wavefunctions. The specific influence of these factors enters through the explicit form of the functions Z_s.

Using Poisson's summation formula, Greenspoon and Pathria (1974) have carried out an asymptotic evaluation of Z_s under periodic boundary conditions, with the result (valid for $L_{1,2,3} \gg \lambda$)

$$Z_s = \frac{L_1L_2L_3}{\lambda^3}\left(\frac{\Gamma(s+\frac{3}{2})}{\Gamma(\frac{3}{2})} g_{s+\frac{3}{2}}(\alpha) + (-1)^s\pi^{1/2}\alpha^{s+\frac{1}{2}}S_1(y_j)\right), \tag{7}$$

where λ $(=\hbar(2\pi/MkT)^{1/2})$ is the mean thermal wavelength of the particles, $g_n(\alpha)$ are the familiar Bose–Einstein functions (see Pathria 1972b) while the function $S_1(y_j)$ is defined by

$$S_n(y_j) = \sum_{q_{1,2,3}=-\infty}^{\infty}{}' \frac{e^{-2R(q)}}{R^n(q)}, \qquad R(q) = (q_1^2y_1^2 + q_2^2y_2^2 + q_3^2y_3^2)^{1/2} \qquad (n = 0, \pm1, \pm2, \ldots), \tag{8}$$

where

$$y_j = \pi^{1/2}\alpha^{1/2}(L_j/\lambda) \qquad (j = 1, 2, 3). \tag{9}$$

It will be noted that the primed summation in (8) implies that the term with $q_1 = q_2 = q_3 = 0$ is excluded. From Z_s, one readily obtains asymptotic expressions for other relevant functions, such as G_s, G_s', etc.

Now, for a given geometry, special events associated with the phenomenon of Bose–Einstein condensation take place at distinct, characteristic values of the thermogeometric parameters y_j, which depend only on the shape of the system and not on its actual size. Greenspoon and Pathria (1974) have considered two such events, namely the maximum in the specific heat C_V of the system and the minimum in the second temperature derivative of the chemical potential μ. The characteristic equations locating these macroscopic events turn out to be

$$\frac{1 + S_0 + 2S_{-1}}{(1+S_0)^3} = \frac{10\pi}{3}\frac{\zeta(\frac{5}{2})}{(\zeta(\frac{3}{2}))^3} \tag{10}$$

and

$$2S_{-2}(1+S_0) - 3S_{-1}(1 + S_0 + 2S_{-1}) = 0, \tag{11}$$

respectively. The resulting values of $y_<$ (the smallest of the y_j) for three leading geometries, along with the values corresponding to $T = T_0(\infty)$, are displayed in the top three rows of table 1. These values can be converted into the corresponding characteristic temperatures T with the help of the asymptotic relationship

$$\frac{T}{T_0(\infty)} = 1 + \tfrac{2}{3}(\zeta(\tfrac{3}{2}))^{-2/3}\left(\frac{\bar{l}}{L_<}y_<\right)(2 - S_1). \tag{12}$$

Table 1. Characteristic values of the thermogeometric parameter $y_<$ for various cuboidal geometries.

	'Transition point'	Nature of criterion	Reference	Thin film $(\infty \times \infty \times L)$	Square channel $(\infty \times L \times L)$	Cube $(L \times L \times L)$
1	$y_<(T_0(\infty))$		Greenspoon and Pathria (1974)	0·481†	0·756	0·970
2	$y_<((C_V)_{max})$	macroscopic	Greenspoon and Pathria (1974)	0·85	1·14	1·35
3	$y_<((\partial^2\mu/\partial T^2)_{min})$	macroscopic	Greenspoon and Pathria (1974)	1·72	1·856	1·987
4	$y_<((y_l^{-1})_{IP})$	macroscopic		—‡	—‡	1·241
5	$y_<((y_l^{-1})_{INT})$	macroscopic		—‡	—‡	3·524
6	$y_<((K_{y_l})_{max})$	macroscopic		0·396‖	0·912	1·245
7	$y_<((K_{y_l^{-1}})_{max})$	macroscopic		1·251	1·652	2·087
8	$y_<((K_f)_{max})$	hybrid	Goble and Trainor (1966)	—‡	—‡	1·962
9	$(y_<)_K$	hybrid	Krueger (1968)	—§	—§	$\pi/\gamma^{1/2}$
10	$y_<((N_1)_{max})$	microscopic	Landsberg (1954)	—§	—§	$O(N^{-1/12})$
11	$(y_<)_{OS}$	microscopic	Osborne (1949)	$O(N^{-1/6})$	$O(N^{-1/6})$	$O(N^{-1/6})$

† This result may be stated explicitly as $\sinh^{-1}(\frac{1}{2}) \equiv \ln[\frac{1}{2}(\sqrt{5}+1)] = 0{\cdot}4812$.
‡ No solution exists such that $y_< = O(1)$.
‖ This result may be stated explicitly as $\sinh^{-1}\{[2(a^2+1)]^{-1/2}\} \equiv \ln\{[1+(2a^2+3)^{1/2}][2(a^2+1)]^{-1/2}\} = 0{\cdot}3962$, where a is given by equation (17).
§ The criterion in question applies only to a completely finite geometry, such as a cube.

3. Other macroscopic criteria

Greenspoon and Pathria (1975) have pointed out a straightforward relation between the thermogeometric parameters y_j and the bulk correlation length ξ:

$$y_j = \tfrac{1}{2}(L_j/\xi). \tag{13}$$

This suggests that y_j^{-1}, which is directly proportional to ξ, might be of a more direct significance than y_j itself. In the light of this we have studied the temperature dependence of both y_j and y_j^{-1}, in the hope of evolving another possible criterion for the onset of Bose–Einstein condensation in a finite system. For this, we decided to look at: (i) the point of inflection, which also leads to the intercept of the tangent at the point of inflection; and (ii) the maximum of the curvature of y_j and y_j^{-1} as functions of temperature. For (ii), we found it preferable to employ the scaled temperature variables (Barber and Fisher 1973)

$$z_j = (L_j/\bar{l})(\hat{T}-1) \qquad (j=1,2,3) \tag{14}$$

instead of $\hat{T}$ itself, where $\hat{T} = T/T_0(\infty)$. Following the procedure of § 2, the characteristic equations for (i) and (ii) turned out to be

$$S_{-1} = 0 \tag{15a}$$

$$(1+S_0)[(1+S_0)S_{-2} - 3S_{-1}^2] + a^2 S_{-2} = 0 \tag{15b}$$

for y_j, and

$$1 + S_0 - S_{-1} = 0 \tag{16a}$$

$$(1+S_0)[2S_{-2}(1+S_0) - 3S_{-1}^2 - 3(1+S_0-S_{-1})^2] + (a^2/y_<^4)(3+3S_0-6S_{-1}+2S_{-2}) = 0 \tag{16b}$$

for y_j^{-1}; here,

$$a = \tfrac{3}{4}(\zeta(\tfrac{3}{2}))^{2/3} \simeq 1{\cdot}4226. \tag{17}$$

We find that (15a) has no solutions such that $y_< = O(1)$; (16a) has a solution only for a cubic geometry (see row four of table 1), the corresponding characteristic temperature $\hat{T}$ being greater than unity. The $\hat{T}$ intercept of the tangent at the point of inflection is also greater than one; the y value corresponding to this intercept is given in row five of table 1. Equations (15b) and (16b) have also been solved for the three geometries considered here and the resulting $y_<$ values are displayed in rows six and seven, respectively, of table 1.

According to Ziman (1953) and Goble and Trainor (1966), the finite analogue T_L of London's (1938) bulk transition temperature $T_0(\infty)$ may be obtained by setting the chemical potential μ, which appears in the expression for the number of particles, $N_{exc}(\mu, T)$, in all the excited states of the system, equal to the ground-state energy ϵ_0 and equating the resulting expression to the total number N. Strictly speaking, $\mu = \epsilon_0$ only at $T=0$, at which point it is N_0, rather than N_{exc}, which is equal to N. This procedure leads to a finite T_L simply because one generally employs an approximate expression for the function $N_{exc}(\mu, T)$. Clearly, this cannot provide a proper criterion for the onset of superfluidity in a finite system.

4. Hybrid and microscopic criteria

The singular behaviour of the condensate fraction $f(=N_0/N)$ in an infinite system is well known:

$$f(\hat{T})=\begin{cases}1-\hat{T}^{3/2} & (\hat{T}\leqslant 1)\\ 0 & (\hat{T}>1).\end{cases} \tag{18}$$

In a finite system, however, $f(\hat{T})$ varies smoothly with $\hat{T}$ (see figure 1). Goble and Trainor (1966) have suggested two possible criteria based on the behaviour of the function $f(\hat{T})$: (i) the $\hat{T}$ intercept of the tangent at the point of inflection of $f(\hat{T})$; and (ii) the point of maximum curvature of $f(\hat{T})$.

We obtain, for the point of inflection of the condensate fraction $f(\hat{T})$, the characteristic equation

$$3S_0-2S_{-1}+3=0. \tag{19}$$

We find that this equation has no solution for the cubic geometry such that $y_{\mathrm{IP}}=\mathrm{O}(1)$, so we consider instead the possibility that $y_{\mathrm{IP}}\ll 1$. Assuming y_{IP} to be $\mathrm{O}(N^n)$, we obtain, after a rather lengthy calculation,

$$\left(\frac{\partial^2 f}{\partial\hat{T}^2}\right)\simeq-\frac{3N_0(N_0+1)\zeta(\frac{3}{2})y^4}{4\pi^2N\hat{T}^2}\left(\frac{L}{\lambda}\right)^{-1}\times\begin{cases}1 & (-\frac{1}{6}\leqslant n<-\frac{1}{18})\\ 1-\dfrac{6D_4y^6}{\pi^5}\zeta(\frac{3}{2})\left(\dfrac{L}{\lambda}\right) & (n=-\frac{1}{18})\\ -\dfrac{6D_4y^6}{\pi^5}\zeta(\frac{3}{2})\left(\dfrac{L}{\lambda}\right) & (-\frac{1}{18}<n<0),\end{cases} \tag{20}$$

where (Zucker 1975, Zasada and Pathria 1976)

$$D_4={\sum_{l_{1,2,3}=-\infty}^{\infty}}'\frac{1}{(l_1^2+l_2^2+l_3^2)^2}\simeq 16{\cdot}53232. \tag{21}$$

The point of inflection is therefore given by

$$y_{\mathrm{IP}}=(\pi^5/6D_4\zeta(\tfrac{3}{2}))^{1/6}(\lambda/L)^{1/6}=\mathrm{O}(N^{-1/18}) \tag{22}$$

and, correspondingly, $f_{\mathrm{IP}}=\mathrm{O}(N^{-2/9})$. The corresponding temperature $\hat{T}_{\mathrm{IP}}$ turns out to be

$$\hat{T}_{\mathrm{IP}}\simeq 1-(16D_4/9\pi^2)^{1/3}(\zeta(\tfrac{3}{2}))^{-4/9}N^{-2/9}, \tag{23}$$

which is less than one.

Similar analysis for the thin-film and square-channel geometries shows that there is no inflection point for $f(\hat{T})$ within the foregoing range of $y_<$. This means that the inflection point for these geometries, if it exists, lies so close to $\hat{T}=0$ that the condition $(\lambda/L_<)\ll 1$ is no longer satisfied and hence our mathematical formulation becomes inapplicable.

Going back to the cubic geometry, we obtain for the $\hat{T}$ intercept of the tangent at the point of inflection (see figure 1)

$$\hat{T}_{\mathrm{INT}}\simeq 1+\tfrac{2}{3}(16D_4/9\pi^2)^{2/3}(\zeta(\tfrac{3}{2}))^{-8/9}N^{-4/9}, \tag{24}$$

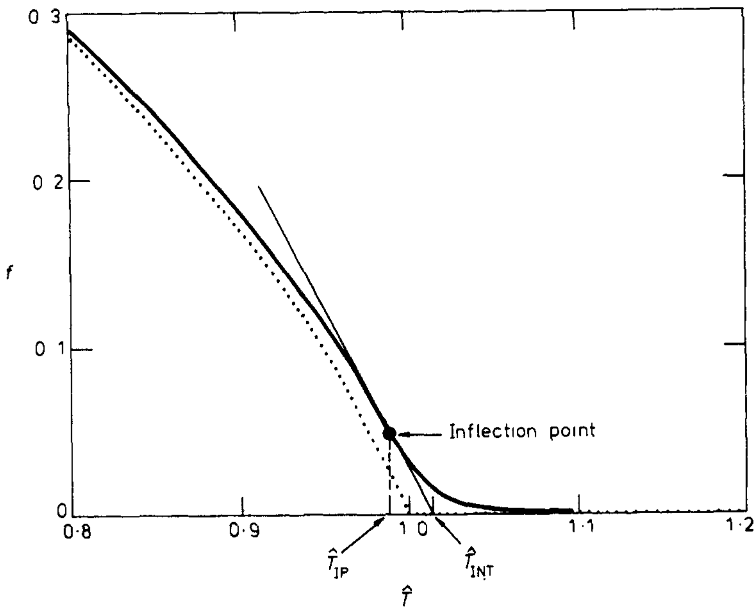

Figure 1. Schematic diagram showing the condensate fraction f as a function of $\hat{T}$, for fixed N and L_j. Dotted curve, infinite system; full curve, finite cubic geometry under periodic boundary conditions.

which agrees with the behaviour shown by the actual condensate fraction curves obtained numerically by Zasada and Pathria (1976).

We now look at the point of maximum curvature in the $f(\hat{T})$ curve. After a lengthy calculation we arrive at the characteristic equation for this point, namely

$$(1+S_0)[(1+S_0)(S_{-2}-\tfrac{3}{2}S_{-1})-3(1+S_0-S_{-1})^2]$$
$$+(9\pi^2/16y_<^6N^2)(L_</\bar{l})^6(15+15S_0-18S_{-1}+4S_{-2})=0. \qquad (25)$$

For the cubic geometry the solution is $y = 1{\cdot}962$; again, for the thin-film and square-channel geometries there are no solutions such that $y_< = O(1)$. These results are shown in row eight of table 1.

Krueger (1968) proposed the requirement that

$$N_0/N_1 = 1+\gamma \qquad (26)$$

where $\gamma = O(1)$; Krueger himself worked with $\gamma = 1$. Equation (26) implies that

$$\alpha \simeq \beta\epsilon_1/\gamma = O(N^{-2/3}) \qquad (27)$$

and hence

$$(y_j)_K = \pi L_j/\gamma^{1/2}L_> = O(1); \qquad (28)$$

here, $L_>$ is the length of the largest side of the container. From (28) it follows that Krueger's criterion can be applied only to a completely finite geometry, such as a cube (see row nine of table 1).

Another criterion, a microscopic one, considered by Landsberg (1954) and by Goble and Trainor (1966), is based on the behaviour of the mean occupation number

N_1 of the first excited state of the system. Since, for an unambiguous definition of the first excited state, the system must be finite in all of its dimensions, we may restrict ourselves to a cubic geometry here. The state in question is then sixfold degenerate and has an energy $\epsilon_1 = \hbar^2/2ML^2$. The criterion now consists in locating the temperature at which the occupancy of the energy level ϵ_1 passes through a maximum. This leads to the condition

$$G_1/G_0 = \pi(\lambda/L)^2. \tag{29}$$

We find that this equation has no solutions such that $y = O(1)$. However, if we consider $y \ll 1$, we do find a solution (see row ten of table 1), namely

$$y((N_1)_{\max}) = [2\pi^3/3\zeta(\tfrac{3}{2})]^{1/4}(\lambda/L)^{1/4} = O(N^{-1/12}) \tag{30}$$

and, correspondingly, $f = O(N^{-1/6})$. The corresponding characteristic temperature is given by

$$\hat{T}((N_1)_{\max}) \simeq 1 - (2/3\pi)^{1/2}(\zeta(\tfrac{3}{2}))^{-1/3}N^{-1/6}, \tag{31}$$

which is again less than one. It is readily seen that if we considered an excited state other than the first we would obtain essentially the same results as in (30) and (31), only with somewhat different numerical factors.

Finally, we note that Osborne (1949) introduced the concept of an accumulation temperature T_a as the temperature at which a finite fraction of particles begins to accumulate in a single state (or set of states with the same energy). By a finite fraction Osborne meant 'less than, but not a great deal less than, unity or very much greater than $1/N$'. At this temperature one would have

$$(y_j)_{\text{OS}} = (\pi/rN)^{1/2}(L_j/\lambda) = O(N^{-1/6}); \tag{32}$$

here, r is a fraction of order 1. The foregoing result is included in row eleven of table 1.

5. Conclusions

We are now in a position to comment on the relative merits and demerits of the different criteria investigated. The most suitable criteria would be those which: (i) are applicable to all geometries; and (ii) give 'transition points' within a specific range of $y_<$ for all geometries. For instance, condition (i) eliminates the criterion proposed by Krueger while condition (ii) eliminates the curvature maximum of the condensate fraction f. The criteria which survive this screening process are: (a) the point at which the specific heat is a maximum; (b) the point at which the second temperature derivative of the chemical potential is a minimum; and (c) the points corresponding to the maximum curvature of y_j and y_j^{-1}. However, the latter were derived with the help of the scaling variables z_j. It will be noted that the use of slightly different scaling variables, say $z_j' = 2z_j$, would still give transition points such that $y_< = O(1)$ but numerically they would be different from the ones appearing in rows seven and eight of table 1. This arbitrariness makes the use of these points unsuitable as a possible criterion. Another survivor of the screening process is Osborne's proposal of an accumulation temperature T_a. However, due to the arbitrariness associated with the unspecified value of r in equation (32), this leads to a broad range of $y_<$ values rather than a definite point.

Of the criteria (a) and (b), the second one does not correspond to a directly observable physical event. Consequently, the most useful general criterion for the onset of Bose–Einstein condensation in finite systems seems to be the macroscopic one based on the specific-heat maximum.

Our results for the 'transition point' fall into two distinct categories: $y_< = O(1)$ and $y_< = O(N^n)$, with $-\frac{1}{6} \leq n < 0$ (see table 1). Since $y_<$ is a monotonic function of $\hat{T}$, a perusal of these results gives us a fairly good idea of the relative ordering of the various 'transition points' that emerged in this study. However, the pattern varies somewhat from one geometry to another. Moreover, one wonders how the various results would be affected if one chose boundary conditions other than periodic.

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