DETERMINING THE CHEMICAL POTENTIAL
OF CONFINED QUANTUM SYSTEMS OF BOSONIC
AND FERMIONIC TYPE

NICHOLAS IONESCU-PALLAS, OVIDIU RACOVEANU, VALENTIN I. VLAD
Institute of Atomic Physics, NIPNE-Dept. Lasers, Romanian Academy – CASP, Bucharest, Romania

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Abstract. The relationship, expressing the particle number parameter of a confined quantum
system (for instance an ideal bosonic or fermionic gas) in terms of the chemical potential, may be
considered as an integral equation for determining the fugacity. Fugacity is obtained as infinite series
in the increasing powers of the particle number, which is strongly convergent for the entire range of
the thermodynamic parameters, including the region of the so called Bose-Einstein condensation. The
asymptotic behavior of the expansion coefficients for increasing ordering number is studied and a
simple rule for it is discovered.

Key words: chemical potential, bosons, fermions, chemical systems.

By studying the ideal quantum gases (in an infinite volume), either of
fermionic or of bosonic type, we come across the following normalization integral
[1–10]:

\[ y = \frac{2}{\sqrt{\pi}} \int_{0}^{\infty} x \sqrt{u} e^{u \pm x} du, \]  

(1)

with the known notations for fugacity: \( x = \exp(\frac{\mu}{k_B T}) \) and for the particle
number: \( y = (p_p \cdot \lambda_T^3) / g_s \), \( \mu \) being the chemical potential, \( p_p \) the particle density,
\( g_s \) the spin weight \( (g_s = 2S + 1) \), \( T \) the absolute temperature, and
\( \lambda_T = h / (2\pi m_0 k_B T)^{1/2} \) – “de Broglie” wavelength associated to the thermal
agitation. The double sign \( \pm \) stands for specifying the belonging to a definite kind
of statistics (plus, for fermions, whose spin is half-integral and minus, for bosons,
whose spin is integral).

We may distinguish two kinds of problems, coming from the normalization integral (1): either to calculate \( y \) \( (i.e., \) the particle number) when \( x \) \( (i.e., \) the
fugacity) is given, or to calculate \( x \), when \( y \) is given. Formally, the first and the
second (the inverse) problem are solved by resorting to infinite series:
The expansion $y(x)$ for bosons is restricted to the range $x \in (0, 1)$. In this case, $x(y)$ is obtained as an alternative and strongly convergent series:

$$x(y) = +1.000\,000\,000\,000\,0 - 0.353\,553\,390\,6\,y^2 + 0.057\,549\,910\,3\,y^3 - 0.005\,763\,960\,4\,y^4 + 0.004\,014\,949\,4\,y^5 - 0.000\,020\,981\,9\,y^6 + 0.000\,000\,860\,2\,y^7 - 0.000\,000\,028\,6\,y^8 + 0.000\,000\,000\,8\,y^9.$$

So, the problem of normalization for bosons is solved in this stage of investigation and further efforts are to be paid only for fermions. Both series, $y(x)$ and $x(y)$, must be processed in this case for being convenient to numerical computation. The series $x(y)$ is convergent for any $y$, provided that we have an analytical expression for $a(y)$ or, alternatively, a recursive relationship for generating the set $a(j)$.

The first 15 coefficients $a(j)$, $j = 1, 2, 3, \ldots, 15$ were directly calculated, by performing partial derivatives against $y$ of the equation $\frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x(y)\sqrt{u}}{u + x(y)} du - y = 0$ and by accounting for few rules given below

$$x'(y) = I_2(x), \quad \frac{d}{dx} I_k(x) = \pm k I_{k+1}(x),$$

$$\frac{d}{dy} \left[ I_k(x) \right]^n = \pm nk \frac{(I_k)^{n-1} \cdot (I_{k+1})}{I_2},$$

$$I_k(x) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{e^u\sqrt{u}}{(e^u \pm x)^k} du, \quad I_k(0) = (k-1)^{-3/2}, \quad k \geq 2.$$

We obtain:

$$y(x) = 2 \sqrt{\frac{x}{\pi \sqrt{x}}} \int_0^\infty e^{x(u - x)}, \quad x(y) = \sum_{j=0}^{j-1} \frac{x^j}{j!}.$$
An inconvenient feature of the method is the fact that the quantity $a(j)$ is obtained as the difference between two quantities approaching rapidly one to another. For instance

\[
\begin{align*}
a_8 &= 4.315 \, 064 \, 051 \, 367 \, 664 \, \ldots - 4.315 \, 064 \, 022 \, 720 \, 515 \, \ldots - \\
a_9 &= 8.895 \, 117 \, 309 \, 023 \, 917 \, \ldots - 8.895 \, 117 \, 308 \, 228 \, 634 \, \ldots - \\
a_{10} &= 18.701 \, 986 \, 107 \, 733 \, 463 \, \ldots - 18.701 \, 986 \, 107 \, 714 \, 688 \, \ldots - .
\end{align*}
\]

Owing to this peculiarity, the calculation of $a(j)$ for $j = 15$ becomes very difficult, and we prefer to extrapolate the data obtained for $1 \leq j \leq 15$.

\[
\begin{align*}
a_1 &= 1 \\
a_2 &= 0.353 \, 553 \, 390 \, 593 \, 273 \, 762 \, 200 \, 422 \, 181 \, 052 \\
a_3 &= 0.0 \, 575 \, 499102 \, 701 \, 247 \, 451 \, 636 \, 170 \, 731 \, 66 \\
a_4 &= 5.763 \, 960 \, 400 \, 910 \, 254 \, 403 \, 418 \, 852 \, 781 \, 95 \times 10^{-3} \\
a_5 &= 4.019 \, 494 \, 151 \, 523 \, 009 \, 595 \, 556 \, 172 \, 119 \, 66 \times 10^{-4} \\
a_6 &= 2.098 \, 189 \, 887 \, 226 \, 047 \, 990 \, 544 \, 860 \, 297 \, 42 \times 10^{-5} \\
a_7 &= 8.602 \, 131 \, 084 \, 260 \, 305 \, 660 \, 043 \, 913 \, 343 \, 16 \times 10^{-7} \\
a_8 &= 2.864 \, 714 \, 862 \, 376 \, 648 \, 729 \, 368 \, 242 \, 210 \, 25 \times 10^{-8} \\
a_9 &= 7.952 \, 831 \, 467 \, 852 \, 416 \, 890 \, 194 \, 817 \, 612 \, 25 \times 10^{-10} \\
a_{10} &= 1.877 \, 442 \, 591 \, 005 \, 677 \, 562 \, 204 \, 988 \, 130 \, 99 \times 10^{-11} \\
a_{11} &= 3.824 \, 796 \, 826 \, 418 \, 090 \, 295 \, 924 \, 653 \, 344 \, 69 \times 10^{-13} \\
a_{12} &= 6.843 \, 294 \, 301 \, 019 \, 079 \, 985 \, 788 \, 027 \, 623 \, 03 \times 10^{-15} \\
a_{13} &= 1.076 \, 210 \, 409 \, 305 \, 379 \, 172 \, 455 \, 417 \, 733 \, 81 \times 10^{-16} \\
a_{14} &= 1.512 \, 411 \, 021 \, 619 \, 883 \, 691 \, 059 \, 052 \, 478 \, 13 \times 10^{-18} \\
a_{15} &= 2.071 \, 573 \, 879 \, 297 \, 704 \, 362 \, 793 \, 713 \, 783 \, 63 \times 10^{-20}.
\end{align*}
\]

For extrapolating the set $a(j)$ at higher values of the ordering number $j$, we must first to temperate the strong decrease of $a(j)$ by suitable transformations. The most convenient transformation, so far discovered, is the following one:

\[
x'(0) = I_2^{-1}(0) = 1, \quad x''(0) = \pm \frac{I_3(0)}{I_2^3(0)} = \pm \frac{1}{\sqrt{2}}
\]

\[
x'''(0) = -6 \left[ \frac{I_4(0)}{I_2^2(0)} - 2 \frac{I_5^2(0)}{I_2(0)} \right] = \left( \frac{3}{2} - \frac{2}{\sqrt{3}} \right) \ldots \text{etc.}
\]
The recursive equation (8) may be integrated to deliver the formula:

\[
\ln \frac{1}{a(k)} = \tilde{A}_0 + \sum_{j=1}^{j=k-1} \ln \left( j + \frac{1}{2} \right) + \sum_{s=1}^{s=6} \tilde{A}_s \cdot \sum_{j=1}^{j=k-1} \ln \left( j + \frac{1}{2} \right), \quad a(1) = 1
\]  

(9)

Asking the recovering of the first terms, \( \ln \frac{1}{a(k)} \) \( k = 2, 3 \ldots 7 \), previously determined by the derivative method, this time by using formula (9), we obtain for the coefficients the values:

\[
\begin{align*}
\tilde{A}_0 &= 1.5665402 \\
\tilde{A}_3 &= 5.282907 \\
\tilde{A}_1 &= 1.0055233 \\
\tilde{A}_4 &= 6.4879443 \\
\tilde{A}_2 &= 1.2988561 \\
\tilde{A}_5 &= 4.7150408.
\end{align*}
\]  

(10)

For \( k \gg 1 \), the sums in (9) may be approximated by using an Euler & Mac Laurin type formula:

\[
\sum_{j=1}^{j=k-1} h\left( j + \frac{1}{2} \right) = \int_1^k h(x) dx + \text{Const.} - \frac{1}{24} h'(k) + \frac{7}{5760} h''(k) - \ldots
\]  

(11)

So, we get the asymptotic expression for \( f(k) \equiv \ln \frac{1}{a(k)} \) as:

\[
f(k) = A_0 \left( k \ln k - k + \frac{1}{k} \right) + A_1 \left( \ln k \right)^2 + A_2 \left( 1 - \frac{1}{k} \right) + A_3 \frac{\ln k}{k} + \\
+ A_4 \left( 1 - \frac{1}{k^2} \right) + A_5 \frac{\ln k}{k^2}.
\]  

(12)

For extending the domain of applicability of the above formula towards small \( k \), we asked first the fulfillment of the condition \( f(1) = 0 \). Thereafter, we preferred to determine the coefficients \( (A_0, A_s) \) directly from the numerical data, rather than from the previous coefficients \( (\tilde{A}_0, \tilde{A}_s) \). In this way, the error made by neglecting the higher terms in the summation formula (9) is, to a great extent, compensated. Accordingly, the coefficients in (12) are the following ones.
Formula (12) with coefficients (13) gives accurate values of \( a(k) \) for small \( k \) (\( k = 1\pm 10 \)). For \( k > 10 \), the respective formula may be used in conjunction with 'saddle-point' method (s.p.m.). According to this approximation method, we may write:

\[
S(y) \equiv \sum_{k=1}^{\infty} a(k) y^k \approx \int_{1/2}^{\infty} \exp \left[ k \ln y - f(k) \right] dk \approx y^{k_0} \cdot e^{-f(k_0)}. 
\]

From (12)–(15), we conclude that the expression of \( f(k) \) does hold in the range \( y = 0\pm 10^3 \), i.e. in the range \( x = 0\pm 3.2 \times 10^{32} \). Within this impressive domain of validity, the error is continuously increasing, reaching a maximal value of about 17% for \( y = 10^3 \).

Further on, we slightly decreased the value of \( A_0 \) and, at the same time, determined the other coefficients of the formula through the condition of exactly reproducing \( f(2) \), \( f(3) \), \ldots \( f(6) \). The effect of this mathematical handling is the reducing of the error for \( y = 10^3 \) at the expense of an increase of the curvature over the entire range of \( y \). Accordingly, the values of the coefficients become:

\[
\begin{align*}
A_0 &= 1.5650437 & A_3 &= 4.4012254 \\
A_1 &= 0.5320747 & A_4 &= -5.4689789 \\
A_2 &= 6.3133160 & A_5 &= +2.2030869.
\end{align*}
\]

The numerical situation is now as follows:

\[
\begin{array}{cccccccc}
 y & k_0 & a(k_0) & S(y)_{s,p.m.} & S(y)_{asympt.} \\
200 & 27.343926 & 1.0873608 \times 10^{-46} & 9.7035967 \times 10^{17} & 8.8743 \times 10^{17} \\
600 & 56.875819 & 1.6030756 \times 10^{-122} & 2.5192943 \times 10^{37} & 2.2256 \times 10^{37} \\
800 & 68.765256 & 2.5619225 \times 10^{-156} & 1.8504401 \times 10^{45} & 1.7572 \times 10^{45} \\
900 & 74.307584 & 1.4976249 \times 10^{-172} & 8.7369671 \times 10^{48} & 8.7354 \times 10^{48} \\
1000 & 79.635229 & 2.0545182 \times 10^{-188} & 2.9974679 \times 10^{52} & 3.1841 \times 10^{52}.
\end{array}
\]
The last improvement we bring to this approximation method is the reducing discrepancy between $S(y)_{s.p.m.}$ and $S(y)_{asympt}$. In this purpose, we made the conjecture that the unknown value of the coefficient $\tilde{a}(k)$, taken in the saddle point $k_0$, is displaced, as compared to the calculated value $a(k)$, taken in the same point, in a proportion determined by the ratio $S_{asympt}/S_{s.p.m.}$.

$$\tilde{a}(k_0) = a(k_0) \frac{S_{asympt}}{S_{s.p.m.}}.$$  \hfill (18)

As a result of this conjecture, the values of $a(k_0)$ in (17) are changed by resorting to formula (18). Therefore, we re-determine the coefficients in (12) by making a least square adjustment of the respective formula through the following points

<table>
<thead>
<tr>
<th>$k$</th>
<th>$f(k)$</th>
<th>$k$</th>
<th>$f(k)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.0397208</td>
<td>9</td>
<td>20.952323</td>
</tr>
<tr>
<td>3</td>
<td>2.8551027</td>
<td>10</td>
<td>24.698526</td>
</tr>
<tr>
<td>4</td>
<td>5.1561305</td>
<td>27.343926</td>
<td>105.92450</td>
</tr>
<tr>
<td>5</td>
<td>7.8191843</td>
<td>43.467689</td>
<td>197.41438</td>
</tr>
<tr>
<td>6</td>
<td>10.771851</td>
<td>56.875819</td>
<td>280.56741</td>
</tr>
<tr>
<td>7</td>
<td>13.966086</td>
<td>68.765256</td>
<td>358.31422</td>
</tr>
<tr>
<td>8</td>
<td>17.368212</td>
<td>74.307584</td>
<td>395.64154</td>
</tr>
</tbody>
</table>

The coefficients so determined are:

$$A_0 = 1.557395 \quad A_3 = 28.630420$$

$$A_1 = 0.809094 \quad A_4 = -46.268444$$

$$A_2 = 42.913809 \quad A_5 = 23.961319.$$  \hfill (19)

The effect of correcting the curvature is in the expected sense:

<table>
<thead>
<tr>
<th>$y$</th>
<th>$S(y)_{s.p.m.}$</th>
<th>$S(y)_{asympt.}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>$8.83865 \times 10^{17}$</td>
<td>$8.8743 \times 10^{17}$</td>
</tr>
<tr>
<td>400</td>
<td>$3.16065 \times 10^{28}$</td>
<td>$3.1562 \times 10^{28}$</td>
</tr>
<tr>
<td>600</td>
<td>$2.25406 \times 10^{37}$</td>
<td>$2.2256 \times 10^{37}$</td>
</tr>
<tr>
<td>800</td>
<td>$1.78505 \times 10^{45}$</td>
<td>$1.7572 \times 10^{45}$</td>
</tr>
<tr>
<td>900</td>
<td>$8.84813 \times 10^{48}$</td>
<td>$8.7354 \times 10^{48}$</td>
</tr>
<tr>
<td>1000</td>
<td>$3.20584 \times 10^{52}$</td>
<td>$3.1841 \times 10^{52}$</td>
</tr>
</tbody>
</table>
In conclusion, the chemical potential was determined as an infinite series in the increasing powers of the particle number, strongly convergent for the whole range of the thermodynamic parameters, including the region of Bose-Einstein condensation [11–17]. The results are used in the calculation of the statistical properties of the confined quantum gases [18]. The asymptotic behavior of the expansion coefficients for increasing ordering number was demonstrated to follow a simple rule.

REFERENCES