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

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Abstract. The relationship, expressing the particle number parameter of a confined quantum system (for instance an ideal bosonic or fermionic gase) 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]:

$$y = \frac{2}{\sqrt{\pi}} \cdot \int_0^\infty \frac{x\sqrt{u}}{e^u \pm x} du, \tag{1}$$

with the known notations for fugacity: $x = \exp\left(\mu / k_B T\right)$ and for the particle number: $y = \left(\rho_p \cdot \lambda_T^3\right) / g_s$, μ being the chemical potential, ρ_p the particle density, g_s the spin weight ($g_s = 2S + 1$), T the absolute temperature, and $\lambda_T = h / \left(2\pi m_0 k_B T\right)^{1/2}$ –"de Broglie" wavelength associated to the thermal agitation. The double sign (±) 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:

$$y(x)=\frac{2}{\sqrt{\pi}}\int_0^{\infty}\frac{x\sqrt{u}}{e^u \pm x}du, \qquad y=\frac{2}{\sqrt{\pi}}\int_0^{\infty}\frac{x(y)\sqrt{u}}{e^u \pm x(y)}du,$$

$$y(x)=\sum_{j=1}^{j=\infty}(\pm 1)^{j-1}\cdot\frac{x^j}{j^{3/2}}, \qquad x(y)=\sum_{j=1}^{j=\infty}(\pm 1)^{j-1}\cdot a(j)\cdot y^j .$$

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:

$$\begin{aligned} x(y) = &+1.\,000\,000\,000\,0\, y - \\ &-0.\,353\,553\,390\,6\, y^2 + \\ &+0.\,057\,549\,910\,3\, y^3 - \\ &-0.\,005\,763\,960\,4\, y^4 + \\ &+0.\,000\,401\,949\,4\, y^5 - \\ &-0.\,000\,020\,981\,9\, y^6 + \\ &+0.\,000\,000\,860\,2\, y^7 - \\ &-0.\,000\,000\,028\,6\, y^8 + \\ &+0.\,000\,000\,000\,8\, y^9. \end{aligned} \qquad 0 \le y \le \zeta(3/2) = 2.6123754 \tag{3}$$

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 $\underline{y}$, 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 $\frac{2}{\pi}\int_0^{\infty}\frac{x(y)\sqrt{u}}{u+x(y)}du - y = 0$ and by accounting for few rules given below

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

$$\frac{d}{dy}\left[I_k(x)\right]^n = \pm nk\frac{(I_k)^{n-1}\cdot(I_{k+1})}{I_2}, \tag{4}$$

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

We obtain:

$$x'(0) = I_2^{-1}(0) = 1, \qquad x''(0) = \pm 2\frac{I_3(0)}{I_2^3(0)} = \pm\frac{1}{\sqrt{2}}$$
$$x'''(0) = -6\left[\frac{I_4(0)}{I_2^4(0)} - 2\frac{I_3^2(0)}{I_2^5(0)}\right] = \left(\frac{3}{2} - \frac{2}{\sqrt{3}}\right) \text{... etc.} \tag{5}$$

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

$$\begin{aligned} a_8 &= 4.315\,064\,051\,367\,664 \ldots - 4.315\,064\,022\,720\,515 \ldots - \\ a_9 &= 8.895\,117\,309\,023\,917 \ldots - 8.895\,117\,308\,228\,634 \ldots - \\ a_{10} &= 18.701\,986\,107\,733\,463 \ldots - 18.701\,986\,107\,714\,688 \ldots -. \end{aligned} \tag{6}$$

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

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

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:

$$\frac{a(k)}{a(k+1)} = \left(k+\frac{1}{2}\right)^{\alpha(k)},$$
$$\alpha(k) = \tilde{A}_0 + \frac{\tilde{A}_1}{\left(k+\frac{1}{2}\right)} + \frac{\tilde{A}_2}{\left(k+\frac{1}{2}\right)^2} + \frac{\tilde{A}_3}{\left(k+\frac{1}{2}\right)^3} + \frac{\tilde{A}_4}{\left(k+\frac{1}{2}\right)^4} + \frac{\tilde{A}_5}{\left(k+\frac{1}{2}\right)^5}. \tag{8}$$

The recursive equation (8) may be integrated to deliver the formula:

$$\ln\frac{1}{a(k)} = \tilde{A}_0 \sum_{j=1}^{j=k-1} \ln\left(j+\frac{1}{2}\right) + \sum_{s=1}^{s=5} \tilde{A}_s \cdot \sum_{j=1}^{j=k-1} \frac{\ln\left(j+\frac{1}{2}\right)}{\left(j+\frac{1}{2}\right)^s}, \quad a(1) = 1 \tag{9}$$

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

$$\begin{aligned} \tilde{A}_0 &= 1.5665402 & \tilde{A}_3 &= 5.282907 \\ \tilde{A}_1 &= 1.0055233 & \tilde{A}_4 &= 6.4879443 \\ \tilde{A}_2 &= 1.2988561. & \tilde{A}_5 &= 4.7150408. \end{aligned} \tag{10}$$

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

$$\sum_{j=1}^{j=k-1} h\left(j+\frac{1}{2}\right) = \int_1^k h(x)\,dx + Const. - \frac{1}{24}h'(k) + \frac{7}{5760}h'''(k) - .... \tag{11}$$

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

$$f(k) = A_0\left(k\ln k - k + \frac{1}{k}\right) + A_1(\ln k)^2 + A_2\left(1-\frac{1}{k}\right) + A_3\frac{\ln k}{k} + \\ + A_4\left(1-\frac{1}{k^2}\right) + A_5\frac{\ln k}{k^2}. \tag{12}$$

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 $\left(\tilde{A}_0, \tilde{A}_s\right)$. 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.

$$
\begin{aligned}
&A_0 = 1.5658093 \qquad A_3 = 4.1414758 \\
&A_1 = 0.5244859 \qquad A_4 = 5.1292496 \\
&A_2 = 6.0438311 \qquad A_5 = 2.0513211.
\end{aligned} \tag{13}
$$

Formula (12) with coefficients (13) gives accurate values of $a(k)$ for small k ($k = 1\div10$). For $k > 10$, the respective formula may be used in conjuction with 'saddle-point' method (s.p.m.). According to this approximation method, we may write:

$$
\begin{aligned}
S(y) \equiv \sum_{k=1}^{k=\infty} a(k) y^k \approx \int_{1/2}^{\infty} \exp\left[k \ln y - f(k)\right] dk \approx y^{k_0} \cdot e^{-f(k_0)} \cdot \\
\cdot \int_{-\infty}^{+\infty} e^{-\frac{1}{2} f''(k_0)\xi^2} d\xi = \sqrt{\frac{2\pi}{f''(k_0)}} \cdot y^{k_0} \cdot e^{-f(k_0)}.
\end{aligned} \tag{14}
$$

Here, the saddle point k_0 is defined through the condition:

$$
f'(k_0) - \ln y = 0. \tag{15}
$$

From (12)–(15), we conclude that the expression of $f(k)$ does hold in the range $y = 0\div10^3$, *i.e.* in the range $x = 0\div3.2 \times 10^{52}$. 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:

$$
\begin{aligned}
&A_0 = 1.5650437 \qquad A_3 = 4.4012254 \\
&A_1 = 0.5320747 \qquad A_4 = -5.4689789 \\
&A_2 = 6.3133160 \qquad A_5 = +2.2030869.
\end{aligned} \tag{16}
$$

The numerical situation is now as follows:

y	k_0	$a(k_0)$	$S(y)_{s.p.m.}$	$S(y)_{asympt.}$
200	27.343926	$1.0873608 \times 10^{-46}$	9.7035967×10^{17}	8.8743×10^{17}
600	56.875819	$1.6030756 \times 10^{-122}$	2.5192943×10^{37}	2.2256×10^{37}
800	68.765256	$2.5619225 \times 10^{-156}$	1.8504401×10^{45}	1.7572×10^{45}
900	74.307584	$1.4967249 \times 10^{-172}$	8.7369671×10^{48}	8.7354×10^{48}
1000	79.635229	$2.0545182 \times 10^{-188}$	2.9974679×10^{52}	3.1841×10^{52}.

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 $S_{asympt.}/\ S_{s.p.m.}$.

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

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

k	$f(k)$	k	$f(k)$
2	1.0397208	9	20.952323
3	2.8551027	10	24.698526
4	5.1561305	27.343926	105.92450
5	7.8191843	43.467689	197.41438
6	10.771851	56.875819	280.56741
7	13.966086	68.765256	358.31422
8	17.368212	74.307584	395.64154
		79.635229	432.10556.

(19)

The coefficients so determined are:

$$A_0 = 1.557395 \qquad A_3 = 28.630420$$
$$A_1 = 0.809094 \qquad A_4 = -46.268444$$
$$A_2 = 42.913809 \qquad A_5 = 23.961319.$$

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

y	$S(y)_{\text{s.p.m.}}$	$S(y)_{\text{asympt.}}$
200	8.83865×10^{17}	8.8743×10^{17}
400	3.16065×10^{28}	3.1562×10^{28}
600	2.25406×10^{37}	2.2256×10^{37}
800	1.78505×10^{45}	1.7572×10^{45}
900	8.84813×10^{48}	8.7354×10^{48}
1000	3.20584×10^{52}	3.1841×10^{52}

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.

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