DEVELOPMENT OF PARTITION FUNCTION IN BOLTZMANN DISTRIBUTION
VI. FORMULA FOR LN Z

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Summations of the previously obtained infinite series to a closed formula for the partition function Z in the quasi-ideal approximation are performed for some values of the parameters. It is proved that the formula for $\ln Z$ as a function of temperature exhibits one point of discontinuity.

In the calculation of the grand-canonical partition function Z of a system of interacting particles a formula for $\ln Z$ containing all the terms up to infinite order in perturbation which are leading in the Boltzmann approximation of quantum expressions, has been obtained [1]. The formula has been written in a form containing an infinite series, and it seemed to be impossible to sum it up to any simple function. It has, however, been proved that this series is convergent within a finite radius. Yet, in this paper we shall present a method of the summation of $\ln Z$ to a closed formula containing no infinite series, for some values of the parameters. This is of some importance because (i) the closed form is much simpler for any calculations and, moreover, (ii) the obtained formulas show without doubt the possibility of existence of a discontinuous point in $\ln Z$ as the function of temperature, whereas in the foregoing form it could have always been suspected that the explicitly written singularities might eventually be cancelled out by some terms of the infinite series.

1. Summation of $\ln Z$

We start from the equation (IV.5.4) of [1], expressing the contribution to $\ln Z$ from all the possible leading diagrams containing at least two W-interactions (we write it here, for the sake of simplicity, in a slightly modified form)

$$\overline{W}(\beta) \equiv -\frac{\beta A}{F}\{W(\beta)-W_1(\beta)\} = \sum_{k=1}^{\infty}\sum_{i=k+1}^{\infty}\frac{1}{i!}D^k E^{i-k+1}\Gamma(k, i), \tag{1.1}$$

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where, according to (III.4.1),

$$\Gamma(k, i) = \binom{i}{k-1} \sum_{s=0}^{k-1} (-1)^s \binom{k-1}{s} (k-s)^{i-2}. \tag{1.2}$$

It has been shown in [1], part II that for $k = i-1$,

$$\Gamma(k, k+1) = \Gamma(i-1, i) = \frac{1}{2} i! = \frac{1}{2}(k+1)!. \tag{1.3}$$

We can also prove (*cf.* Appendix) that for $k = i-2$,

$$\Gamma(k, k+2) = \frac{1}{2} \cdot \frac{1}{3!} (k+2)!\, k(k+1). \tag{1.4}$$

These two relations will be useful in further calculations.

Let us now rearrange the triple summations in (1.1) in a fashion similar to that used in Eqs (IV. 5.4)—(IV. 5.9) of [1]. We have, step by step,

$$\overline{W}(\beta) = \sum_{k=1}^{\infty} \sum_{i=k+1}^{\infty} \sum_{s=0}^{k-1} \frac{1}{(i-k+1)!} \frac{(-1)^s}{s!(k-1-s)!} (k-s)^{i-2} D^k E^{i-k+1}$$

$$= \sum_{k=1}^{\infty} \sum_{j=2}^{\infty} \sum_{s=0}^{k-1} \frac{(-1)^s}{j!\, s!} \frac{(k-s)^{j+k-3}}{(k-s-1)!} D^k E^j$$

$$= \sum_{s=0}^{\infty} \sum_{l=0}^{\infty} \sum_{j=2}^{\infty} \frac{(-1)^s}{j!\, s!\, l!} (l+1)^{j-2+l+s} E^j D^{l+s+1}$$

$$= \sum_{k=1}^{\infty} \sum_{j=2}^{\infty} \frac{1}{j!\,(k-1)!} k^{j+k-3} E^j (De^{-D})^k \tag{1.5}$$

$$= \sum_{k=1}^{\infty} \frac{k^{k-3}}{(k-1)!} (De^{-D})^k (e^{kE} - kE - 1), \tag{1.5'}$$

and the series (1.5′) has been proved in [1], Part IV to be convergent at least for

$$|De^{1+E-D}| < 1, \ |De^{1-D}| < 1. \tag{1.6}$$

We now introduce the relation (1.3) into (1.1) and perform the same rearrangements. We get

$$\overline{W}(\beta) = \frac{E^2}{2!} \sum_{k=1}^{\infty} D^k + \sum_{k=1}^{\infty} \sum_{i=k+2}^{\infty} \frac{1}{i!} D^k E^{i-k+1} \Gamma(k, i)$$

$$= \frac{E^2}{2!} \frac{D}{1-D} + \sum_{k=1}^{\infty} \frac{k^{k-3}}{(k-1)!} (De^{-D})^k \left(e^{kE} - \frac{1}{2!} k^2 E^2 - kE - 1\right), \tag{1.7}$$

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which proves the relation (compare with (1.5'))

$$y_1 \equiv \sum_{k=1}^{\infty} \frac{k^{k-1}}{(k-1)!} (De^{-D})^k = \frac{D}{1-D}. \tag{1.8}$$

Introducing now the relation (1.4) into (1.7), we get

$$\overline{W}(\beta) = \frac{E^2}{2!}\frac{D}{1-D} + \frac{E^3}{3!}\sum_{k=1}^{\infty}\binom{k+1}{2} D^k + \sum_{k=1}^{\infty}\sum_{i=k+3}^{\infty}\frac{1}{i!} D^k E^{i-k+1}\Gamma(k, i)$$
$$= \frac{E^2}{2!}\frac{D}{1-D} + \frac{E^3}{3!}\frac{D}{(1-D)^3} +$$
$$+ \sum_{k=1}^{\infty}\frac{k^{k-3}}{(k-1)!}(De^{-D})^k\left(e^{kE} - \frac{1}{3!}k^3E^3 - \frac{1}{2!}k^2E^2 - kE - 1\right), \tag{1.9}$$

which proves the relation

$$y_2 \equiv \sum_{k=1}^{\infty}\frac{k^k}{(k-1)!}(De^{-D})^k = \frac{D}{(1-D)^3}. \tag{1.10}$$

Let us note that the relation (1.10) can be obtained from the relation (1.8) in the following way:

Denote

$$z \equiv De^{-D}. \tag{1.11}$$

Thus

$$y_1 = \sum_{k=1}^{\infty}\frac{k^{k-1}}{(k-1)!} z^k = \frac{D}{1-D},$$

$$y_2 = \sum_{k=1}^{\infty}\frac{k^k}{(k-1)!} z^k = z\sum_{k=1}^{\infty}\frac{k^{k-1}}{(k-1)!} kz^{k-1} = z\frac{d}{dz}\sum_{k=1}^{\infty}\frac{k^{k-1}}{(k-1)!} z^k$$
$$= z\frac{d}{dz}\frac{D}{1-D} = \frac{D}{1-D}\frac{d}{dD}\frac{D}{1-D} = \frac{D}{(1-D)^3}, \tag{1.12}$$

which agrees with (1.10). In general,

$$y_n = \sum_{k=1}^{\infty}\frac{k^{k+n-2}}{(k-1)!} z^k = z\frac{d}{dz} y_{n-1} = \left(\frac{D}{1-D}\frac{d}{dD}\right)^{n-1}\frac{D}{1-D}. \tag{1.13}$$

The form (1.5) of $\overline{W}(\beta)$ can be written in terms of the quantities y_n, which permits by the use of (1.13) the summations to be performed formally to the end,

$$\overline{W}(\beta) = \sum_{j=2}^{\infty}\frac{E^j}{j!} y_{j-1} = \int_0^1 dx_1 \int_0^{x_1} dx \sum_{j=2}^{\infty} E^j \frac{x^{j-2}}{(j-2)!}\left(\frac{D}{1-D}\frac{d}{dD}\right)^{j-2}\frac{D}{1-D}$$
$$= E^2 \int_0^1 dx_1 \int_0^{x_1} dx \exp\left(\frac{xED}{1-D}\frac{d}{dD}\right)\frac{D}{1-D}. \tag{1.14}$$

The formula for ln Z in the approximation of leading terms of the Boltzmann expansion (the quasi-ideal approximation) is, after minor rearrangements (compare with [1], Eqs (IV. 2.5), (IV. 3.8))

$$\ln Z = Fe^{-\beta B}\left\{1+\beta A+\frac{1}{2}D+\frac{1}{D}\overline{W}(\beta)\right\}. \tag{1.15}$$

The above form proves the existence in ln Z of a discontinuity point located at $D = 1$.

The form (1.14) is, however, nothing but the compact way of writing of an infinite series, and thus it is not well suited for either detailed calculations of the equation of state, *etc.*, or a discussion of the behaviour of the $D = 1$ singularity. For these purposes, the summations of (1.14) for some special cases will be performed.

Write the explicit values of the first few coefficients y_n:

$$y_1 = \frac{D}{1-D}, \quad y_2 = \frac{D}{(1-D)^3}, \quad y_3 = \frac{D}{(1-D)^5}(1+2D),$$

$$y_4 = \frac{D}{(1-D)^7}(1+8D+6D^2), \quad y_5 = \frac{D}{(1-D)^9}(1+22D+58D^2+24D^3), \ldots$$

$$y_n = \frac{D}{(1-D)^{2n-1}}[1+\ldots+(n-1)!\,D^{n-2}], \tag{1.16a}$$

or, in other form,

$$y_1 = \frac{D}{1-D}, \quad y_2 = \frac{D}{(1-D)^2}\left[1+\left(\frac{D}{1-D}\right)\right],$$

$$y_3 = \frac{D}{(1-D)^3}\left[1+4\left(\frac{D}{1-D}\right)+3\left(\frac{D}{1-D}\right)^2\right],$$

$$y_4 = \frac{D}{(1-D)^4}\left[1+11\left(\frac{D}{1-D}\right)+25\left(\frac{D}{1-D}\right)^2+3\cdot 5\left(\frac{D}{1-D}\right)^3\right],$$

$$y_5 = \frac{D}{(1-D)^5}\left[1+26\left(\frac{D}{1-D}\right)+130\left(\frac{D}{1-D}\right)^2+210\left(\frac{D}{1-D}\right)^3+3\cdot 5\cdot 7\left(\frac{D}{1-D}\right)^4\right]$$

$$y_n = \frac{D}{(1-D)^n}\left[1+\ldots+1\cdot 3\cdot 5\cdot\ldots(2n-3)\left(\frac{D}{1-D}\right)^{n-1}\right]. \tag{1.16b}$$

Thus, for $|D| \ll 1$,

$$y_n \approx D/(1-D)^{2n-1} \approx D, \qquad |D| \ll 1, \tag{1.17}$$

and

$$\overline{W}(\beta) \approx D(1-D)^3(e^R-R-1) \approx D(e^E-E-1),\ R = E/(1-D)^2. \tag{1.18}$$

For $|D| \gg 1$,

$$y_n \approx \frac{(n-1)!\,D^{n-1}}{(1-D)^{2n-1}} \approx \frac{(n-1)!\,(-1)^{2n-1}}{D^n}, \qquad |D| \gg 1, \tag{1.19}$$

$$\overline{W}(\beta) \approx \frac{E}{D}(1-D)\left\{1 + \left[\frac{(1-D)^2}{DE} - 1\right] \ln\left[1 - \frac{DE}{(1-D)^2}\right]\right\} \tag{1.20a}$$

$$\approx -E+\beta A(1-\beta B)\ln(-\beta A), \tag{1.20b}$$

where the relations: $E = D+\beta A$, $D = -\beta A\, e^{-\beta B}$ have been used. (*cf.* [1]). Note that $A < 0$ if $|D| \gg 1$, and $V > 0$. The above formulas permit the calculations of the equation of state, *etc.*, to be performed in a simple way in two limiting cases, $|D| \ll 1$, and $|D| \gg 1$.

For the discussion of the behaviour of the partition function near the singular point, the case $D \to 1$ is to be examined. In this case, $D/(1-D) \gg 1$, and

$$y_1 = \frac{D}{1-D}, \qquad y_n \approx (2n-3)!!\,(1-D)\left[\frac{D}{(1-D)^2}\right]^n, \qquad n = 2, 3, \ldots, \tag{1.21}$$

$$\overline{W}(\beta) \approx \frac{1}{2}\frac{DE^2}{1-D} + \frac{(1-D)^3}{D}\sum_{j=3}^{\infty}\frac{(2j-5)!!}{j!}\left[\frac{DE}{(1-D)^2}\right]^j \tag{1.22a}$$

$$= \frac{DE^2}{1-D}\left\{\frac{1}{2} + \sum_{j=3}^{\infty}\frac{1}{j!}\frac{(2j-4)!}{(j-2)!}\left[\frac{DE}{2(1-D)^2}\right]^{j-2}\right\}$$

$$= \frac{DE^2}{1-D}\left\{\frac{1}{2} + \int_0^1 dz_1 \int_0^{z_1} dz\, \frac{\partial}{\partial x}\sum_{j=1}^{\infty}\frac{(-1)^j}{j!}\left(\frac{\partial}{\partial x}\right)^{j-1}\left[-\frac{DEzx^2}{2(1-D)^2}\right]^j\right\}_{x=1}. \tag{1.22b}$$

Now, according to the well-known Lagrange theorem, the series

$$\mu = x + \sum_{k=1}^{\infty}\frac{(-1)^k}{k!}\left(\frac{\partial}{\partial y}\right)^{k-1}[M(y)]^k|_{y=x} \tag{1.23}$$

is the expansion solution of the functional equation

$$\mu = x - M(\mu). \tag{1.24}$$

Thus, in (1.22b),

$$\sum_{j=1}^{\infty}\frac{(-1)^j}{j!}\left(\frac{\partial}{\partial x}\right)^{j-1}\left[-\frac{DEzx^2}{2(1-D)^2}\right]^j = \frac{(1-D)^2}{DEz}\left[1 \pm \sqrt{1 - \frac{2DEzx}{(1-D)^2}}\right] - x, \tag{1.25}$$

and

$$\overline{W}(\beta) \approx \mp E(1-D) \pm \frac{(1-D)^3}{3D} \mp \frac{1}{3D}[(1-D)^2 - 2DE]^{3/2}, \tag{1.26}$$

which is finite for $D \to 1$. Note that this solution is meaningful for $DE < 0$ only. On the other hand, for $DE > 0$, the series (1.22a) diverges for $D \to 1$, because it is given by the sum of positive terms, each of which separately is infinitely large in this limit. The above describes the behaviour of $\ln Z$ near the point $D = 1$: $\ln Z$ is singular at this point only if $DE > 0$.

2. *Introduction of the exchange corrections*

According to the results of the Part V of this series of publications [1], the so-called exchange corrections, which take into account the quantum effects during collisions of the particles, can be introduced into the expression (1.16) for $\ln Z$ by writing (we write it for $D \ll 1$)

$$\ln Z = \sum_{\boldsymbol{p}} f_{\boldsymbol{p}} e^{-\beta B_{\boldsymbol{p}}} \left\{1+\beta A_{\boldsymbol{p}}+\frac{1}{2} D_{\boldsymbol{p}}+(1-D_{\boldsymbol{p}})^3 (eR_{\boldsymbol{p}}-R_{\boldsymbol{p}}-1)\right\}, \tag{2.1}$$

where

$$A_{\boldsymbol{p}} = A \mp \sum_{\boldsymbol{q}} v(\boldsymbol{q}) f_{\boldsymbol{p}+\boldsymbol{q}}, \qquad B_{\boldsymbol{p}} = V+A_{\boldsymbol{p}}$$

$$D_{\boldsymbol{p}} = -\beta A_{\boldsymbol{p}} e^{-\beta B_{\boldsymbol{p}}}, \quad E_{\boldsymbol{p}} = -\beta A_{\boldsymbol{p}}(e^{-\beta B_{\boldsymbol{p}}}-1), \quad R_{\boldsymbol{p}} = E_{\boldsymbol{p}}/(1-D_{\boldsymbol{p}})^2, \tag{2.2}$$

and for the temperatures for which the thermal de Broglie wavelength Λ is much smaller than the range σ of the intermolecular forces, $A_{\boldsymbol{p}}$ can be approximated by

$$A_{\boldsymbol{p}} = A \mp V f_{\boldsymbol{p}}, \qquad \Lambda \ll \sigma. \tag{2.3}$$

These corrections change also the location and the behaviour of the singular point in $\ln Z$, as it has been pointed out in the preceeding part of this work.

3. *Quasi-ideal equation of state*

The relatively simple forms (1.18), (1.20b) of $\ln Z$ enable us to write the equation of state of a quasi-ideal gas in an also relatively simple form (for special values of the parameter D). It is well-known (*cf. e. g.* [2]) that the pressure P of the system is related to $\ln Z$ by

$$\frac{P\Omega}{kT} = \ln Z, \tag{3.1}$$

(Ω is the volume of the system) and that in order to obtain the equation of state, the chemical potential μ' or the fugacity $e^{\alpha'}$ is to be eliminated from (3.1), and the average number of particles $\mathcal{N}$ is to be introduced into (3.1) by means of the relation

$$\mathcal{N} = \left(\frac{\partial \ln Z}{\partial \alpha'}\right)_{\beta, \Omega}. \tag{3.2}$$

Nore that

$$f_{\boldsymbol{p}} = e^{\alpha' -\beta V-\beta \varepsilon_{\boldsymbol{p}}}, \qquad F = \sum_{\boldsymbol{p}} f_{\boldsymbol{p}}, \tag{3.3}$$

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so that we get from (1:18), for $D \ll 1$

$$\mathcal{N} = Fe^{-\beta B}\{1+E(1-\beta A)+(1-\beta A)(1-4D)(1-D)^2(e^R-R-$$

$$-1+[D+\beta A-\beta AD^2-2(\beta A)^2D+D^2](e^R-1)\}. \tag{3.4}$$

Both (3.4) and (1.16) are complicated functions of $e^{\alpha'}$. However, this complication can be removed by the following procedure. The parameter A can be written

$$A = 2wF = \frac{\lambda}{\Omega}v(0)\cdot e^{\beta V}\mathcal{N}_{id}, \tag{3.5}$$

where

$$\mathcal{N}_{id} = \sum_p e^{\alpha'-\beta\varepsilon_p} = \sum_q \langle N_p\rangle_{o'}, \tag{3.6}$$

is the average number of particles as calculated for an ideal (non-modified — compare with [1], Parts I, V) gas. Thus $\mathcal{N}_{id}$ can be determined from the ideal gas equation of state, $P\Omega = \mathcal{N}_{id}kT$, and

$$A = a\cdot e^{\beta V}\beta P = a\cdot e^{V/kT}P/kT, \qquad a \equiv \lambda v(0), \tag{3.5a}$$

where the potential parameter a is no longer dependent of the temperature, pressure, volume, *etc.* The fortunate feature of Eqs (3.4) and (1.16) is that the factors $e^{\alpha'}$ appear within the curly brackets in combinations with the potential parameter w only. The quasi-ideal equation of state is then obtained by eliminating from (3.1)—(1.16) the factor $Fe^{-\beta B}$ by means of (3.4), and by expressing the parameters A by (3.5a). The right-hand side of the equation of state obtained in this way is a function of T and P only (and is not a function of volume) and can be further expanded into a virial series of increasing powers of pressure.

In a similar manner the quasi-ideal equation of state containing the exchange correcions can be obtained. The procedure is obvious, and we write the final result, for $D \ll 1$

$$\frac{P\Omega}{\mathcal{N}kT} = \sum_p e^{-\beta(\varepsilon_p+A_p)}\left\{1+\beta A_p+\frac{1}{2}D_p+(1-D_p)^3(e^{R_p}-R_p-1)\right\}\times$$

$$\times\{\sum_p e^{-\beta(\varepsilon_p+A_p)}[1+E_p(1-\beta A_p)+(1-\beta A_p)(1-4D_p)(1-D_p)^2(e^{R_p}-$$

$$-R_p-1)+(D_p+\beta A_p-\beta A_pD_p^2-2\beta^2A_{-p}^2D_p+D_p^2)(e^{R_p}-1)]\}^{-1}, \tag{3.7}$$

where B_p, D_p, E_p, R_p, are given by (2.2), and A_p is to be written in the form (compare with 2.2) and and (3.5a))

$$A_p = ae^{V/kT}\frac{P}{kT}\left\{1\mp\sum_q v(q)e^{-\beta\varepsilon_{p+q}}/v(0)\sum_q e^{-\beta\varepsilon_q}\right\}; \tag{3.8}$$

(r, if the approximation (2.3) holds,

$$A_p = (a\mp V\Lambda^3e^{-\beta\varepsilon_p})e^{V/kT}\frac{P}{kT}. \tag{3.8a}$$

The equation (3.7) can also be expanded into a virial series.

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APPENDIX

We shall prove the formula (1.4) by using the same method by which the formula (1.3) was proved earlier ([1], Part III). Write ($t = k-1$)

$$s^{*}_{t+1} = \sum_{s=0}^{t} (-1)^{s} \binom{t}{s} (t-s+1)^{t+1} = \sum_{s=0}^{t} (-1)^{t-s} \binom{t}{s} (s+1)^{t+1} \tag{A.1}$$

$$= \left[\frac{\partial}{\partial x_1} \cdots \frac{\partial}{\partial x_{t+1}} x_1 \ldots x_{t+1} \sum_{s=0}^{t} (-1)^{t-s} \binom{t}{s} (x_1 \ldots x_{t+1})^{s}_{s}\right]_{x_1=\ldots=x_{t+1}=1}$$

$$= \left[\frac{\partial}{\partial x_1} \cdots \frac{\partial}{\partial x_{t+1}} x_1 \ldots x_{t+1}(x_1 \ldots x_{t+1}-1)^{t}_{t}\right]_{x_1=\ldots=x_{t+1}=1}. \tag{A.2}$$

Differentiation with respect to $x_1, \ldots, x_t$ yields

$$S^{*}_{t+1} = \left[\frac{\partial}{\partial x_{t+1}} \left\{x_{t+1}^{t+1}\, t! + \left(\sum_{i=1}^{t} i\right) t!\, x_{t+1}^{t}(x_{t+1}-1) + \right.\right.$$

$$\left.\left. + \sum_{k=2}^{t} \alpha_k(t)\, x^{t+1-k} (x_{t+1}-1)^{k}\right\}\right]_{x_{t+1}=1}, \tag{A.3}$$

where the values of the coefficients $\alpha_k(t)$ are of no importance for further calculations. The last differentiation gives finally

$$S^{*}_{t+1} = (t+1)! + \binom{t+1}{2} t! = \frac{1}{2}(t+2)!, \tag{A.4}$$

which, together with the formula (1.2), proves the relation (1.4).

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