

# DEVELOPMENT OF PARTITION FUNCTION IN BOLTZMANN DISTRIBUTION V. EXCHANGE CORRECTIONS

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Corrections from the exchange diagrams to the previously obtained formula for the partition function  $Z$  are found. These corrections influence neither the properties of the leading diagrams nor the general form of the expression for  $\ln Z$ . The effect of retaining them results only in a renormalization of the value of the parameter  $A$  of the theory.

In the preceding parts [1] of this work (hereafter they will be referred to as I-IV) the formula for the grand-canonical partition function  $Z$  of a system of interacting particles has been derived in the approximation of the terms leading in the Boltzmann expansion of the quantum-mechanical formula. It is proposed to call this approximation a quasi-ideal one because, for example, the average occupation numbers and the slow neutron cross-section calculated in this way [2] have the same shapes as the respective function for an ideal gas, their temperature and pressure dependence being only altered.

In this part we shall introduce into the obtained formulas the corrections given by terms which are the exchange diagrams with respect to the leading ones. The calculation of these corrections can be performed in a fairly simple way. It is noteworthy that corrections of this type prove to be of importance in the description of the scattering of slow neutrons by real gases [2].

The symbols and notations used throughout are the same as in [1].

## 1. Corrections to $O$ -interactions

In the quasi-ideal approximation discussed in the preceding parts [1] we retained in the formula for  $\ln Z$  the terms containing the parameters

$$F = \sum_{\mathbf{p}} f_{\mathbf{p}}, \quad w = \frac{\lambda}{2\Omega} v(\mathbf{q} = 0), \quad V = \frac{\lambda}{2\Omega} \sum_{\mathbf{q}} v(\mathbf{q}), \quad (1.1)$$

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only. All the terms containing mixed sums and integrals of the potential factors  $v(\mathbf{q})$ , Maxwell-Boltzmann factors  $f_{\mathbf{p}}$ , and temperature integrands, have been neglected there. Now, we shall add to them the terms of the type of

$$\frac{\lambda}{2\Omega} \sum_{\mathbf{p}} \sum_{\mathbf{q}} v(\mathbf{q}) f_{\mathbf{p}} f_{\mathbf{p}+\mathbf{q}}, \quad (1.2)$$

the so-called exchange terms which are usually neglected in the Boltzmann approximation (*cf.*, e.g., [3,4]). These terms describe the quantum-mechanical diffraction effects (manifesting themselves during a collision), and the latter are important when the thermal de Broglie wavelength

$$\Lambda = (2\pi\hbar^2/mkT)^{1/2} \quad (1.3)$$

becomes comparable to, or greater than, the molecular dimensions characterized by the range parameters of the intermolecular potential. Note that in this case we can still approximate the Fermi-Dirac and Bose-Einstein distributions by the Maxwell-Boltzmann distribution  $f_{\mathbf{p}}$ , as the purely "statistics" effects (indistinguishability of particles taken into account in a complete fashion) become important at much lower temperatures (or under higher pressures), when  $\Lambda$  is comparable to, or greater than, the average molecular separation characterized by the density of the gas<sup>1</sup>. This can be expressed formally by admitting that, although terms (1.2) are taken into account, we are still dealing with a system for which

$$f_{\mathbf{p}}^2 \ll f_{\mathbf{p}}. \quad (1.4)$$

Moreover, it shall be shown below (*cf.* Section 5) that the terms (1.2) will give nonvanishing contributions (at least within the expansion scheme used in this work) even if the thermal de Broglie wavelength  $\Lambda$  is much smaller than the range of intermolecular forces.

The inequality (1.4) must be used carefully, however. (1.4) only means that, when eventually all the summations are performed,

$$\sum_{\mathbf{p}} f_{\mathbf{p}}^2 \ll \sum_{\mathbf{p}} f_{\mathbf{p}} = F \sim \mathcal{N}. \quad (1.4a)$$

Yet, we now can not apply the approximation (1.4) everywhere at the beginning, by writing that

$$1 \mp f_{\mathbf{p}} \approx 1,$$

as has been done in quasi-ideal calculations [1] when calculating the value of a contraction

$$\langle a_{\mathbf{p}} a_{\mathbf{q}}^+ \rangle_0 = \delta_{\mathbf{p},\mathbf{q}} (1 \mp f_{\mathbf{p}}) \quad (1.5)$$

(the upper and the lower signs refer always to fermions and bosons, respectively). Let us

<sup>1</sup> For He<sup>4</sup>, for example, the exchange terms become important for temperatures lower than, say, 20°K, whereas the "statistics" effects — below 4.2°K. It must be noted, however, that we use the modified distributions  $f_{\mathbf{p}}$ , being the usual Maxwell-Boltzmann distributions multiplied by exp  $(\beta V)$ , which probably will raise the limits of temperatures in which these effects start to play a role.

take, namely, the complete contribution from an  $O$ -interaction (a first-order term with two internal contractions). We have there two possibilities of total contractions,

$$+0+0 = \sum_{\mathbf{p}} \sum_{\mathbf{k}} \sum_{\mathbf{q}} \tilde{v}(\mathbf{q}) f_{\mathbf{p}} f_{\mathbf{k}} \delta_{\mathbf{q},0} = wF^2, \quad (1.6a)$$

$$\begin{aligned} +0+0 &= \sum_{\mathbf{p}} \sum_{\mathbf{k}} \sum_{\mathbf{q}} \tilde{v}(\mathbf{q}) f_{\mathbf{k}} (1 \mp f_{\mathbf{p}}) \delta_{\mathbf{p}+\mathbf{q},\mathbf{k}} \\ &= VF \mp \sum_{\mathbf{p}} \sum_{\mathbf{q}} \tilde{v}(\mathbf{q}) f_{\mathbf{p}} f_{\mathbf{p}+\mathbf{q}}, \quad \tilde{v} = \frac{\lambda}{2\Omega} v, \end{aligned} \quad (1.6b)$$

and if in the value of the contraction (1.5) the limit  $1 \mp f_{\mathbf{p}} \rightarrow 1$  was taken from the beginning, the term (1.2) would drop out from (1.6b).

Incidentally, we have just calculated the corrected (by the exchange term) value of an  $O$ -interaction:

$$\sum_{\mathbf{p}} [V + wF \mp \sum_{\mathbf{q}} \tilde{v}(\mathbf{q}) f_{\mathbf{p}+\mathbf{q}}] f_{\mathbf{p}}. \quad (1.6c)$$

At the end of this Section, let us note for further purposes that the Fourier-transformed potential  $v(\mathbf{q})$  has the property

$$v(\mathbf{q}) = v(-\mathbf{q}), \quad (1.7)$$

which follows from the hermicity of the Hamiltonian (in fact  $v(\mathbf{q})$  should be taken as the real part of the Fourier transform of the intermolecular potential  $V(\mathbf{r})$ , instead of the Fourier transform itself, at least as long as  $V(\mathbf{r})$  is a real-valued function)<sup>2</sup>.

## 2. Corrections to $T$ -interactions

In a  $T$ -interaction (one internal contraction) we have three possible ways of contracting the single pair of operators which lead to a quasi-ideal contribution, and the fourth possibility which is negligible in that approximation (compare with II, Fig. 5). Now, when the factors of the type of (1.2) are taken into account, this fourth possibility will give a non-vanishing contribution. The first two possibilities are the same as in the quasi-ideal case,

$$(+0+0) + (+0+0) = 2wF \sum_{\mathbf{p}} a_{\mathbf{p}}^+ a_{\mathbf{p}}. \quad (2.1)$$

The third possibility gives an additional contribution, similar to (1.6b),

$$+0+0 = V \sum_{\mathbf{p}} a_{\mathbf{p}}^+ a_{\mathbf{p}} \mp \sum_{\mathbf{p}} \sum_{\mathbf{q}} v(\mathbf{q}) f_{\mathbf{p}+\mathbf{q}} a_{\mathbf{p}}^+ a_{\mathbf{p}}, \quad (2.2)$$

<sup>2</sup> If the property (1.7) is not fulfilled from the beginning,  $v(\mathbf{q})$  can always be symmetrized properly to get eventually (1.7). Note that this can be done, for example, in (1.2) by shifting the dummy indices  $\mathbf{p} \rightarrow \mathbf{p} - \mathbf{q}$ ,  $\mathbf{q} \rightarrow -\mathbf{q}$ .

whereas the fourth possibility leads to the expression

$$\overline{+0+0} = \sum_{\mathbf{p}} \sum_{\mathbf{q}} v(\mathbf{q}) f_{\mathbf{p}+\mathbf{q}} a_{\mathbf{p}} a_{\mathbf{p}}^+ \quad (2.3)$$

According to the definition of a  $T$ -interaction, the creation and annihilation operators standing in (2.1)–(2.3) are to be contracted with the operators belonging to other interactions. Now, the order of operators in (2.3) is reversed as compared with that in (2.1) and (2.2). Using the usual anticommutation/commutation rules for these operators we shall write (2.3) in the form

$$\sum_{\mathbf{p}} \sum_{\mathbf{q}} v(\mathbf{q}) f_{\mathbf{p}+\mathbf{q}} \mp \sum_{\mathbf{p}} \sum_{\mathbf{q}} v(\mathbf{q}) f_{\mathbf{p}+\mathbf{q}} a_{\mathbf{p}}^+ a_{\mathbf{p}} \quad (2.4)$$

The first term of (2.4) vanishes: because it must be contracted with two operators from the other interactions, this will lead to expressions proportional to the averages

$$\langle a_{\mathbf{k}}^+ \rangle_0, \langle a_{\mathbf{k}} \rangle_0 \quad (2.5)$$

which are manifestly zero<sup>3</sup>. The complete contribution — in this approximation — from a  $T$ -interaction is thus

$$(T) = \sum_{\mathbf{p}} [B \mp 2 \sum_{\mathbf{q}} \tilde{v}(\mathbf{q}) f_{\mathbf{p}+\mathbf{q}}] a_{\mathbf{p}}^+ a_{\mathbf{p}}, \quad B = V + 2wF \quad (2.6)$$

### 3. Corrections to $W$ -interactions

It has been found [1] that the quasi-ideal diagrams containing  $W$ -interactions (interactions where all four operators are contracted with operators belonging to other,  $T$ - or  $W$ -interactions) must contain a sufficient number of final  $T$ -chains joined to these  $W$ -interactions. The effect of final  $T$ -chains lies in assuring that in every  $W$ -interaction the momentum change  $\hbar\mathbf{q}_j = 0$ , which effects in the vanishing of the temperature exponentials in temperature integrations. However, for this purpose a second condition must be fulfilled at the same time. Namely, the contraction lines leaving the operators belonging to the same internal pair,  $(a_{\mathbf{p}_j+\mathbf{q}_j} a_{\mathbf{p}_j})$  or  $(a_{\mathbf{k}_j-\mathbf{q}_j} a_{\mathbf{k}_j})$ , within a  $W$ -interaction must go “parallelly” either forming a ring, or entering into a final  $T$ -chain (compare with the “reduction” rules of a  $W$ -diagram in II, Section 5). Because both internal pairs are equivalent with respect to the topological structure of a simplified  $W$ -diagram (cf. II) the physical contribution from every  $W$ -interaction to a quasi-ideal diagram is

$$2wF \quad (3.1)$$

Now, the exchange corrections to (3.1) can be introduced in a similar way as has been done in the preceding Section for the fourth possibility of a  $T$ -interaction. Namely, we

<sup>3</sup> Using the property of trace invariance under cyclic permutations, and the commutation relations for the operators  $a^+$ ,  $a$ , and the ideal density matrix, we get that

$$(1-f_{\mathbf{k}}^{-1}) \langle a_{\mathbf{k}}^+ \rangle_0 = 0, \quad (1-f_{\mathbf{k}}) \langle a_{\mathbf{k}} \rangle_0 = 0,$$

which proves the above statement at least for non-zero temperatures.

shall take into account the possibility that the generalized contraction lines going parallelly in a  $W$ -diagram leave also the "mixed pairs"  $(a_{p_j+q_j}^+ \dots a_{k_j})$  and  $(\dots a_{p_j} a_{k_j-q_j}^+ \dots)$ , all the remaining rules of constructing the diagram being unaltered. It is easy to convince oneself that in this case the temperature exponents remain still equal to zero.

In order to retian the same symbolic picture of such a  $W$ -interaction, we bring together the operators forming mixed pairs, making use of the anticommutation/commutation relations for  $a^+$ ,  $a$  operators, and we get

$$\mp \sum_{\mathbf{p}} \sum_{\mathbf{q}} \sum_{\mathbf{k}} \tilde{v}(\mathbf{q}) a_{\mathbf{p}+\mathbf{q}}^+ a_{\mathbf{k}} a_{\mathbf{k}-\mathbf{q}}^+ a_{\mathbf{p}}, \quad (3.2)$$

plus terms containing a smaller number of creation and annihilation operators. Similarly as the first term of (2.4), the latter give a null contribution.

Now, by inserting (3.2) within a quasi-ideal diagram we get from this "exchange"  $W$ -interaction a contribution

$$\mp 2 \sum_{\mathbf{q}} \tilde{v}(\mathbf{q}) f_{\mathbf{p}+\mathbf{q}} \quad (3.3)$$

and thus the whole "physical" contribution from a  $W$ -diagram will be

$$2[wF \mp \sum_{\mathbf{q}} \tilde{v}(\mathbf{q}) f_{\mathbf{p}+\mathbf{q}}], \quad (3.4)$$

instead of (3.1).

It can be easily checked that *i*) the introduction of the corrected contribution (3.4) does not alter the structure of the whole diagram, and *ii*) there is no other possibility of a linking which would lead to terms proportional to (1.2).

#### 4. Corrections to $\ln Z$

Comparing the corrected expressions (1.6c), (2.6), and (3.4) we conclude that the introduction of exchange terms leads to the "renormalization" of the quasi-ideal parameter  $wF$  to the form

$$wF \rightarrow wF \mp \sum_{\mathbf{q}} \tilde{v}(\mathbf{q}) f_{\mathbf{p}+\mathbf{q}}. \quad (4.1)$$

It has been demonstrated that (*cf.* II, Section 5, IV, Sections 2-4) the whole contribution from a general quasi-ideal diagram is

$$F(2wF)^i B^m = \sum_{\mathbf{p}} f_{\mathbf{p}} (2wF)^i (V + 2wF)^m, \quad (4.2)$$

(*i*, *m*, denote the number of  $W$ - and  $T$ -interactions, forming a diagram, respectively), where the factor  $F = \sum_{\mathbf{p}} f_{\mathbf{p}}$  results from the closed structure of a connected diagram. The renormalization (4.1) implies thus that the retaining of the exchange terms will lead to the renormalized expression

$$\sum_{\mathbf{p}} f_{\mathbf{p}} [2wF \mp 2 \sum_{\mathbf{q}} \tilde{v}(\mathbf{q}) f_{\mathbf{p}+\mathbf{q}}]^i [V + 2wF \mp 2 \sum_{\mathbf{q}} \tilde{v}(\mathbf{q}) f_{\mathbf{p}+\mathbf{q}}]^m = \sum_{\mathbf{p}} f_{\mathbf{p}} A_{\mathbf{p}}^i B_{\mathbf{p}}^m, \quad (4.3)$$

in the place of (4.2). Note that the renormalized contribution (1.6c) from an  $O$ -interaction can be written in the same manner,

$$\sum_{\mathbf{p}} f_{\mathbf{p}} \left( V + \frac{1}{2} A_{\mathbf{p}} \right). \quad (4.4)$$

Therefore, the exchange terms can be introduced into the whole expression (IV. 6.1) in the following fashion:

Write  $\ln Z$  in the form

$$\ln Z = F \cdot \mathcal{L}(A, B) \equiv \sum_{\mathbf{p}} f_{\mathbf{p}} \mathcal{L}(A, B), \quad (4.5)$$

and put

$$A_{\mathbf{p}} \equiv A \mp \frac{2\lambda}{2\Omega} \sum_{\mathbf{q}} v(\mathbf{q}) f_{\mathbf{p}+\mathbf{q}}, \quad B_{\mathbf{p}} \equiv V + A_{\mathbf{p}}, \quad (4.6)$$

instead of  $A, B$ , respectively. The resulting formula,

$$\ln Z = \sum_{\mathbf{p}} f_{\mathbf{p}} \mathcal{L}(A_{\mathbf{p}}, B_{\mathbf{p}}), \quad (4.7)$$

is thus the desired expression for the partition function containing all the quasi-ideal terms plus the exchange corrections to these terms.

It is worth to be noted that the exchange corrections influence the values of the possible points of discontinuity of  $\ln Z$ . The first possible singularity in (4.5) was given by the expression (*cf.* (IV.6.1)).

$$- \frac{1}{2} F e^{-\beta B} [-\beta A (e^{-\beta B} - 1)]^2 (1 + \beta A e^{-\beta B})^{-1}, \quad (4.8)$$

the discontinuity in  $\ln Z$  being located at the point

$$1 + \beta A e^{-\beta B} \equiv 1 - D = 0. \quad (4.9)$$

Introducing the exchange corrections, we get for this term the expression

$$- \frac{1}{2} \sum_{\mathbf{p}} f_{\mathbf{p}} e^{-\beta B_{\mathbf{p}}} [-\beta A_{\mathbf{p}} (e^{-\beta B_{\mathbf{p}}} - 1)]^2 (1 + \beta A_{\mathbf{p}} e^{-\beta B_{\mathbf{p}}})^{-1}, \quad (4.10)$$

which changes manifestly the uncorrected value (4.9) of the first possible discontinuity. Its location is still given by the zero-point of the factor

$$1 + \beta A_{\mathbf{p}} e^{-\beta B_{\mathbf{p}}}, \quad (4.11)$$

but the temperature and the pressure corresponding to this zero-point depend now on the detailed shape of the intermolecular potential. Moreover, the zero-point of (4.11) depends now also on the other factors in (4.10), because of the summation (integration) over the wavevector  $\mathbf{p}$ , which has not been the case in (4.8)–(4.9). Thus the exchange corrections remove the complete separation of different quasi-ideal factors in  $\ln Z$ .

## 5. Estimation of the magnitude of corrections

In order to find the magnitude of the exchange corrections of the type of (1.2), the detailed shape of the potential  $v(\mathbf{q})$  must be known. Terms of this type have been discussed earlier [2] in connection with the scattering of slow neutrons by real gases (by methane under normal conditions). We have used there for the description of the interactions between the methane molecules an analytic potential  $V(\mathbf{r})$ , which possesses an analytic Fourier transform:

$$V(\mathbf{r}) = \varepsilon_1 e^{-(r/\sigma_1)^2} - \varepsilon_2 e^{-(r/\sigma_2)^2}, \quad (5.1)$$

so that

$$v(\mathbf{q}) = \pi^{3/2} [\sigma_1^3 \varepsilon_1 e^{-(q\sigma_1)^2} - \sigma_2^3 \varepsilon_2 e^{-(q\sigma_2)^2}]. \quad (5.2)$$

Thus

$$V = \frac{1}{2} (\varepsilon_1 - \varepsilon_2), \quad w = \frac{\pi^{3/2}}{2\Omega} (\sigma_1^3 \varepsilon_1 - \sigma_2^3 \varepsilon_2), \quad (5.3)$$

and (cf. [2], Part III)

$$\sum_{\mathbf{q}} \tilde{v}(\mathbf{q}) f_{\mathbf{p}+\mathbf{q}} = \frac{1}{2} \pi^{3/2} e^{\alpha' + \beta V} \left\{ \frac{\sigma_1^3 \varepsilon_1 e^{-\mu_1 p^2}}{(\Lambda^2 + \pi\sigma_1^2)^{3/2}} - \frac{\sigma_2^3 \varepsilon_2 e^{-\mu_2 p^2}}{(\Lambda^2 + \pi\sigma_2^2)^{3/2}} \right\}, \quad (5.4)$$

where

$$\mu_i = \frac{\sigma_i^2 \Lambda^2}{4\Lambda^2 + 4\pi\sigma_i^2}, \quad \Lambda^2 = \frac{2\pi\hbar^2}{mkT},$$

and  $e^{\alpha'}$  is the (unmodified) fugacity of the gas. When the thermal de Broglie wavelength  $\Lambda$  is much smaller than the range of intermolecular forces characterized by the parameters  $\sigma_i$  (for methane, e. g., this is the case down to very low temperatures), (5.4) will be simply equal, with good accuracy, to

$$\sum_{\mathbf{q}} \tilde{v}(\mathbf{q}) f_{\mathbf{p}+\mathbf{q}} \approx V f_{\mathbf{p}}, \quad \Lambda^2 \ll \pi\sigma_i^2 \quad (5.4a)$$

This relation should hold independently of the detailed form of the intermolecular potential. (5.4a) shows also that the exchange corrections do not vanish completely at high temperatures. Thus, for not too low temperatures, the corrected values (4.6) of the parameters  $A_{\mathbf{p}}$ ,  $B_{\mathbf{p}}$  will be:

$$A_{\mathbf{p}} = 2wF \mp 2Vf_{\mathbf{p}}, \quad B_{\mathbf{p}} = 2wF + V(1 \mp 2f_{\mathbf{p}}). \quad (5.5)$$

This demonstrates that the exchange corrections are of the order of  $f_{\mathbf{p}}$ . Note that

$$f_{\mathbf{p}} = e^{\alpha' + \beta V - \beta \varepsilon_{\mathbf{p}}}, \quad \varepsilon_{\mathbf{p}} = \frac{\hbar^2 p^2}{2m}, \quad (5.6)$$

or, making use of the normalization (cf. [1], Eq. (I.2.20)) and of the ideal gas equation of state,

$$\sum_{\mathbf{p}} f_{\mathbf{p}} = e^{\beta V} \mathcal{N}_{id}, \quad \mathcal{N}_{id} = \frac{P\Omega}{kT}, \quad (5.7)$$

where  $P$  is the pressure of the gas,

$$e^{\alpha'} = \frac{P}{kT} \quad \text{i. e.,} \quad f_{\mathbf{p}} = \frac{P}{kT} \Lambda^3 e^{(V - \epsilon_{\mathbf{p}})/kT}, \quad (5.8)$$

which increases for decreasing temperature (or for increasing pressure). For methane under normal conditions ( $P = 1$  atm,  $T = 296^\circ\text{K}$ ), the value of  $\exp(\alpha' + \beta V)$  has been estimated to be of the order of  $10^{-2}$  (cf. [2], Eq. (III.3.5)), so that the exchange corrections should be meaningful at temperatures not very much lower than room temperature (and certainly at temperatures near the critical point of the gas) where, however, the approximation (5.4a) will be still satisfactory.

In conclusion, let us note that the purely "quantum-statistical" corrections, mentioned in Section 1, would introduce into (5.5) the terms  $f_{\mathbf{p}}, f_{\mathbf{p}}^2$ , etc. which are much smaller than the exchange corrections because of the absence of the factor  $V$  (or rather  $\beta V$ ), which is rather large. Note that for methane (cf. [2], Part III), the factor  $(V/k)$  has been estimated to be of the order of  $10^3 - 10^4$  °K.

The final values of the corrections introduced into the partition function by the exchange terms will depend on the integrations over the wavevector  $\mathbf{p}$  which must be eventually performed according to (4.7).

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