

# VIRIAL EXPANSION OF MAXWELL-BOLTZMANN DISTRIBUTION OF A REAL GAS

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The Maxwell-Boltzmann distribution of a real gas,  $\langle N(\mathbf{p}) \rangle$  *i.e.*, the probability of finding a particle with momentum  $\hbar\mathbf{p}$  in a system of interacting particles, is calculated in the form of an expansion in powers of the pressure of the gas (the virial expansion). The expansion coefficients are related in a simple way with the usual virial coefficients of the expansion of the equation of state.

It is found that the distribution of momentum remains the same as that for an ideal gas, but the temperature and pressure dependence is changed.

The method of calculating  $\langle N(\mathbf{p}) \rangle$ , both for classical and quantum gases, by means of differentiation of a corresponding expression for the partition function of the system under consideration is used. This method is much simpler than direct calculation of the statistical average of the occupation number operator  $N(\mathbf{p})$  of the momentum eigenstate  $\hbar\mathbf{p}$ .

## 1. Introduction

The true average occupation numbers  $\langle N(\mathbf{p}) \rangle$  of the one-particle eigenstate with momentum  $\hbar\mathbf{p}$  of a system of interacting particles are generalizations — for real systems — of the Fermi-Dirac, Bose-Einstein, or Maxwell-Boltzmann ideal gas distributions. Such quantities are frequently important in many physico-chemical calculations where the number of particles with a given velocity is needed. Moreover, it has been suggested by Balian, Bloch, and de Dominicis [1, 2] that knowledge of the true occupation numbers bears some weight in other statistical-mechanical calculations. It has been also shown that  $\langle N(\mathbf{p}) \rangle$  are closely connected with the description of the scattering of slow neutrons by thermodynamic media [3].

In this paper we shall calculate the average occupation numbers for a gas under “normal” conditions (moderate temperature and pressure) when the quantum effects are negligible, *i. e.*, when the thermal de Broglie wavelength is small in comparison with the range of intermolecular forces, and we shall present  $\langle N(\mathbf{p}) \rangle$  in the form of a power series in pressure (virial expansion).

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$\langle N(\mathbf{p}) \rangle$  can be calculated by means of standard temperature-dependent perturbation techniques as the thermal average of the occupation number operator  $N(\mathbf{p})$  (or as the one-particle density matrix, *cf.* ref. [4]). This is, however, a more difficult task than evaluating the corresponding partition function  $Z$  of the system (*cf.* refs [5] and [6]). We thus propose here a new method of calculating  $\langle N(\mathbf{p}) \rangle$  from a given (presumably known) expression for  $\ln Z$ , which, in the author's opinion, seems to be much simpler than making a direct evaluation of  $\langle N(\mathbf{p}) \rangle$ . This method is quite general, but is especially well-suited for calculating the virial expansion of the classical distribution.

## 2. Differentiation of $\ln Z$ with respect to $\varepsilon_{\mathbf{p}}$

The Hamiltonian of the system is written in its usual form as a sum  $H_0$  of the one-particle kinetic energy operators, and the interaction part  $H_i$ ,

$$H = H_0 + \lambda H_i, \quad H_0 = \sum_{\mathbf{q}} \varepsilon_{\mathbf{q}} N(\mathbf{q}), \quad (2.1)$$

where  $\lambda$  is the coupling constant,  $\varepsilon_{\mathbf{q}} = (\hbar \mathbf{q})^2 / 2m$  is the kinetic energy of the particle characterized by the momentum eigenvalue  $\hbar \mathbf{q}$ , and  $N(\mathbf{q})$  denotes the operator of the number of particles occupying the state  $\hbar \mathbf{q}$ . The detailed form of the  $H_i$  operator is of no importance for the general result. The grand-canonical partition function, and the average  $\langle N(\mathbf{p}) \rangle$  can be written as (*cf.* refs. [1, 2, 4, 5, 7])

$$Z = \text{Tr} e^{\alpha N - \beta H}, \quad \langle N(\mathbf{p}) \rangle = Z^{-1} \text{Tr} e^{\alpha N - \beta H} N(\mathbf{p}). \quad (2.2)$$

The Hamiltonian  $H_0$  explicitly contains the  $N(\mathbf{q})$  operators; thus the simplest way of finding  $\langle N(\mathbf{p}) \rangle$  from the known explicit expression for  $Z$  seems to be by differentiation of  $Z$  with respect to the kinetic energy  $\varepsilon_{\mathbf{q}}$ . Indeed, by analogy to the known relation for  $\langle H_i \rangle$  (*cf.* ref. [2], p. 31, and ref. [8]), and making use of the property of the cyclic invariance of the trace operation, we easily find that

$$\langle N(\mathbf{p}) \rangle = -\beta^{-1} \left( \frac{\partial \ln Z(\varepsilon_{\mathbf{p}})}{\partial \varepsilon_{\mathbf{p}}} \right)_{\alpha, \beta}. \quad (2.3)$$

The relation (2.3) permits to find the average occupation numbers  $\langle N(\mathbf{p}) \rangle$  from the partition function written explicitly as a function of the kinetic energies  $\varepsilon_{\mathbf{q}}$ . This method, however, has one inconvenience<sup>1</sup>. If one uses the perturbation techniques for evaluating  $\ln Z$  (*cf.* any of the quoted references), the quantities  $\varepsilon_{\mathbf{p}}$  will appear not only in the ideal gas distributions  $f_{\mathbf{p}}$ , but also in the integrands of the temperature-integrals of the perturbation series. If we then differentiate the perturbation expansion of  $\ln Z$  term by term, some extra terms which are not present in the direct perturbation expansion of  $\langle N(\mathbf{p}) \rangle$  will appear in every order of the approximation.

<sup>1</sup> This is not the case when the purely classical expressions are considered, because then the free Hamiltonian does not appear in the perturbation series — compare with Eq. (4.1). The method of this Section can thus be used without difficulties in the calculations of Section 5.

Let us illustrate this fact by a simple example. We admit the two-body interactions between the particles:

$$H_i = \sum_{\mathbf{p}} \sum_{\mathbf{k}} \sum_{\mathbf{q}} \tilde{v}(\mathbf{q}) a_{\mathbf{p}+\mathbf{q}}^+ a_{\mathbf{p}}^+ a_{\mathbf{k}-\mathbf{q}}^+ a_{\mathbf{k}}, \quad (2.4)$$

where  $\tilde{v}(\mathbf{q})$  is the Fourier transform of the interaction potential, divided by the double volume, and  $a^+$ ,  $a$  denote the creation and annihilation operators of the free-particle eigenstate ( $N(\mathbf{p}) = a_{\mathbf{p}}^+ a_{\mathbf{p}}$  in this formalism). Moreover, for the sake of simplicity, we consider only the Boltzmann limit of the one-particle distributions,

$$f_{\mathbf{p}} = \text{Tr } e^{\alpha N - \beta H_0} N(\mathbf{p}) / \text{Tr } e^{\alpha N - \beta H_0} \rightarrow e^{\alpha - \beta \epsilon_{\mathbf{p}}} \ll 1, \quad (2.5)$$

$f_{\mathbf{p}}$  being now the Maxwell-Boltzmann distribution (in this limit the terms of lowest order in  $f_{\mathbf{p}}$  are only retained).

A typical second-order term of the expansion of  $\ln Z$  in this approximation reads (compare with [5])

$$\lambda^2 \int_0^{\beta} d\beta_1 \int_0^{\beta_1} d\beta_2 \sum_{\mathbf{k}} \sum_{\mathbf{l}} \sum_{\mathbf{q}} |\tilde{v}(\mathbf{q})|^2 e^{(\beta_1 - \beta_2)(\epsilon_{\mathbf{l}+\mathbf{q}} - \epsilon_{\mathbf{l}} + \epsilon_{\mathbf{k}-\mathbf{q}} - \epsilon_{\mathbf{k}})} f_{\mathbf{l}} f_{\mathbf{k}}. \quad (2.6)$$

The differentiation of (2.6) with respect to  $\epsilon_{\mathbf{p}}$  leads to the expression

$$\begin{aligned} & -2\lambda^2 \beta f_{\mathbf{p}} \int_0^{\beta} d\beta_1 \int_0^{\beta_1} d\beta_2 \sum_{\mathbf{k}} \sum_{\mathbf{q}} |\tilde{v}(\mathbf{q})|^2 f_{\mathbf{k}} \exp [(\beta_2 - \beta_1)(\epsilon_{\mathbf{p}+\mathbf{q}} - \epsilon_{\mathbf{p}} + \epsilon_{\mathbf{k}-\mathbf{q}} - \epsilon_{\mathbf{k}})] - \\ & -2\lambda^2 \int_0^{\beta} d\beta_1 \int_0^{\beta_1} d\beta_2 (\beta_2 - \beta_1) \sum_{\mathbf{k}} \sum_{\mathbf{q}} |\tilde{v}(\mathbf{q})|^2 f_{\mathbf{k}} \{ f_{\mathbf{p}} \exp [(\beta_2 - \beta_1)(\epsilon_{\mathbf{p}+\mathbf{q}} - \epsilon_{\mathbf{p}} + \epsilon_{\mathbf{k}-\mathbf{q}} - \epsilon_{\mathbf{k}})] - \\ & \quad - f_{\mathbf{p}+\mathbf{q}} \exp [(\beta_2 - \beta_1)(\epsilon_{\mathbf{p}} - \epsilon_{\mathbf{p}+\mathbf{q}} + \epsilon_{\mathbf{k}-\mathbf{q}} - \epsilon_{\mathbf{k}})] \}, \quad (2.7) \end{aligned}$$

where the terms of higher order in  $f$  are neglected, according to (2.5). On the other hand, the explicit evaluation of the second-order term of the direct expansion of the average  $\langle N(\mathbf{p}) \rangle$  gives only the first term of (2.7), quantities like the second term of (2.7) never appearing in the calculations.

Of course, all these extra terms will vanish when the summation of the whole perturbation series is performed. However, their appearance at every stage of the perturbation calculation makes the method prescribed by the relation (2.3) much less convenient. In the next Section we shall present another method of evaluating  $\langle N(\mathbf{p}) \rangle$  by differentiating  $\ln Z$  with respect to some parameter, which, although artificial at first sight, does not contain any such inconvenience, and can be used when quantum expressions are of interest.

### 3. Differentiation of $\ln Z(\gamma)$

A closer look at expressions (2.6) and (2.7) leads to the conclusion that the extra terms in (2.7) come from the differentiation of the factor  $\exp \{(\beta_2 - \beta_1)(\epsilon_{\mathbf{l}+\mathbf{q}} - \epsilon_{\mathbf{l}} + \epsilon_{\mathbf{k}-\mathbf{q}} - \epsilon_{\mathbf{k}})\}$ , whereas the proper term is given by the derivative of the ideal gas distributions  $f_{\mathbf{k}} f_{\mathbf{l}}$ . This fact implies the following procedure for the derivation of the proper expression for  $\langle N(\mathbf{p}) \rangle$ .

Write the partition function  $Z$  in the form:

$$Z = \text{Tr} e^{\alpha N - \beta H} = \text{Tr} e^{\alpha N - \beta H_0} S(\beta) = \lim_{\gamma \rightarrow 0} \text{Tr} e^{\alpha N - \beta H_0 + \gamma N(\mathbf{p})} S(\beta) = \lim_{\gamma \rightarrow 0} Z_{\mathbf{p}}(\gamma). \quad (3.1)$$

Because  $N(\mathbf{p})$  commutes with both  $H_0$  and  $N$ , we have

$$\left( \frac{\partial \ln Z_{\mathbf{p}}(\gamma)}{\partial \gamma} \right)_{\alpha, \beta} = [Z_{\mathbf{p}}(\gamma)]^{-1} \text{Tr} \{ N(\mathbf{p}) \exp [\alpha N - \beta H_0 + \gamma N(\mathbf{p})] S(\beta) \} \equiv \langle N(\mathbf{p}) \rangle_{\gamma}, \quad (3.2)$$

and

$$\langle N(\mathbf{p}) \rangle = \lim_{\gamma \rightarrow 0} \langle N(\mathbf{p}) \rangle_{\gamma} = \lim_{\gamma \rightarrow 0} \left( \frac{\partial \ln Z_{\mathbf{p}}(\gamma)}{\partial \gamma} \right)_{\alpha, \beta}. \quad (3.3)$$

Thus, we have yet to determine the  $\mathbf{p}$ -modified partition function  $Z_{\mathbf{p}}(\gamma)$ , defined by (3.1). For this purpose, note that the operator  $S(\beta)$  is defined by means of the "normal" density matrix:

$$\exp(\alpha N - \beta H) = \exp(\alpha N - \beta H_0) S(\beta), \quad (3.4)$$

and thus the perturbation expansion of  $S(\beta)$  does not contain the parameter  $\gamma$ . On the other hand, it is easy to establish the contraction theorem [1, 2, 7] for the averages over the ideal gas density matrix modified by the factor  $\exp(\gamma N(\mathbf{p}))$ . Namely, it is easy to see that the general form of this theorem remains unchanged, the values of the simple contractions being only influenced by the presence of this extra factor. Moreover, these values are easily found, by standard techniques (*cf.* [7,9]), to be equal to

$$\langle a_k^+ a_q \rangle_{\gamma} = \frac{\text{Tr} \exp [\alpha N - \beta H_0 + \gamma N(\mathbf{p})] a_k^+ a_q}{\text{Tr} \exp [\alpha N - \beta H_0 + \gamma N(\mathbf{p})]} = \delta_{k,q} f_{\mathbf{q}}(\gamma), \text{ etc.}, \quad (3.5)$$

where

$$f_{\mathbf{q}}(\gamma) = (\exp(-\alpha + \beta \varepsilon_{\mathbf{q}} - \delta_{\mathbf{p}, \mathbf{q}} \gamma) \pm 1)^{-1}, \quad (3.6)$$

are the  $\mathbf{p}$ -modified quantum ideal gas distributions. In the limit of classical systems,

$$f_{\mathbf{q}}(\gamma) \rightarrow e^{\alpha - \beta \varepsilon_{\mathbf{q}}} e^{\gamma \delta_{\mathbf{p}, \mathbf{q}}} = f_{\mathbf{q}} e^{\gamma \delta_{\mathbf{p}, \mathbf{q}}}, \quad (3.7)$$

the  $\mathbf{p}$ -modified Maxwell-Boltzmann distribution.

It results directly from the above that the expression for the  $\mathbf{p}$ -partition function  $Z_{\mathbf{p}}(\gamma)$  is obtained from the corresponding expression for the usual partition function  $Z$  by changing all the ideal gas distributions  $f_{\mathbf{q}}$  into  $\mathbf{p}$ -distributions  $f_{\mathbf{q}}(\gamma)$ . Symbolically,

$$Z_{\mathbf{p}}(\gamma) = Z(f_{\mathbf{q}} \rightarrow f_{\mathbf{q}}(\gamma)). \quad (3.8)$$

Moreover, we have

$$\frac{\partial}{\partial \gamma} f_{\mathbf{q}}(\gamma) = \delta_{\mathbf{p}, \mathbf{q}} f_{\mathbf{q}}(\gamma) [1 \mp f_{\mathbf{q}}(\gamma)], \quad \lim_{\gamma \rightarrow 0} f_{\mathbf{q}}(\gamma) = f_{\mathbf{q}}. \quad (3.9)$$

The formula (3.3), together with the above prescriptions, presents a useful method of evaluating the true occupation numbers by simple differentiation of the corresponding expression for the grand-canonical partition function. Note that by applying this procedure to the term (2.6) we shall immediately get the correct result, *i. e.*, the first term of (2.7), because in this case only the factors  $f_{\mathbf{k}}f_{\mathbf{l}}$  are to be taken into account.

#### 4. Virial expansion of $\ln Z$

The classical method of obtaining the virial expansion of the equation of state of a gas is well known (*cf.* [9, 10]). However, this method cannot be used directly for our present purposes because all the momentum integrations are performed there at the very beginning, and thus no factors like (3.5)–(3.7) appear in the corresponding formula for  $\ln Z$ . We shall then find in this Section the virial expansion of  $\ln Z$  as given by quantum formulas (2.2), (3.1), in the classical limit.

The Hamiltonian of a real gas can be written in the form (2.1)–(2.4) (*cf.* [5]), and the classical limit of the theory means that (i) the relation (2.5) is valid, (ii) we can neglect (in average) the commutator of  $H_0$  and  $H_i$ . Thus the grand-partition function is

$$\begin{aligned} Z &= \text{Tr} \exp(\alpha N - \beta H) \xrightarrow{\text{class. lim.}} \text{Tr} \{ \exp(\alpha N - \beta H_0) \exp(-\beta \lambda H_i) \} \\ &= Z_0 \langle \exp(-\beta \lambda H_i) \rangle. \end{aligned} \quad (4.1)$$

where  $Z_0$  is the grand-partition function of an ideal gas, and the average is taken over the ensemble of non-interacting particles (in the modified sense of ref. [5], because of the form (2.4) of the interaction Hamiltonian).

Now, the average (4.1) can be computed by expanding the exponent into a power series and by applying to the resulting averages the contraction theorem (*cf.* [1, 2, 5, 7, 8]). Moreover, it is almost trivial to find for this case that (4.1) is to be calculated by means of linked diagrams only:

$$\ln Z = \ln Z_0 + \sum_{n=1}^{\infty} \frac{(-\beta \lambda)^n}{n!} \langle H_i^n \rangle_{\text{linked}}. \quad (4.2)$$

It is easy to find by the direct calculus of any one of the terms (*e. g.*, of the second order) of the expansion (4.2), and of the corresponding term of the perturbation expansion of the quantum formula (4.1) (*cf.* [5]) that in the expansion (4.2) the terms are neglected, which are — in comparison with unity — of the order of  $(\Lambda^2/\sigma^2)$  where  $\Lambda$  is thermal de Broglie wavelength, and  $\sigma$  denotes the range of intermolecular forces, characterizing the interaction  $v(\mathbf{q})$ .

For the calculation of (4.2) we shall make use of the simplified diagrams representation of ref. [5]. In these diagrams every block of four creation and annihilation operators belonging to one  $H_i$ , Eq. (2.4), are represented by a point, and the contraction of two operators by a line. The line goes above points if it represents a contraction with a creation operator standing to the left, and below it if a creation operator stands to the right in the contracted pair. Thus, in the classical limit, the upper line is proportional to the Boltzmann factor (3.5)  $\rightarrow$  (3.7), whereas the lower line is proportional to unity.

Let us classify the diagrams according to the number of upper lines. We shall see below that this is equivalent to the classification in powers of the pressure of the gas. Thus

$$\ln Z = \ln Z_0 + \sum_{j=1}^{\infty} Z_j, \tag{4.3}$$

where  $Z_j$  denotes the contribution from all the linked diagrams containing  $j$  upper lines. Examples of diagrams belonging to different  $Z_j$  are shown in Figs. 1-3.

Before writing analytic expressions, let us turn our attention to the problem of final and bounded  $T$ -chains (cf. ref. [5]), partially composing these diagrams. The contribution

$$Z_2 = \infty + \text{diagram 1} + \text{diagram 2} + \text{diagram 3} + \dots,$$

$$\infty = |\overline{+ \circ + \circ}|, \quad \text{diagram 1} = |\overline{+ \circ + \circ} + \overline{+ \circ + \circ}| + |\overline{+ \circ + \circ} + \overline{+ \circ + \circ}|, \text{ etc.},$$

$$\overline{+ \circ} = \langle a_j^+ a_k \rangle_0, \quad \overline{\circ +} = \langle a_j a_k^+ \rangle_0.$$

Fig. 1. The contribution  $Z_2$  from linked diagrams containing two upper lines, and the symbolic expressions for these diagrams: + and  $\circ$  denote the creation and annihilation operators, respectively

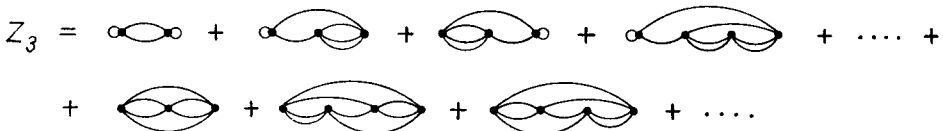


Fig. 2. The contribution  $Z_3$

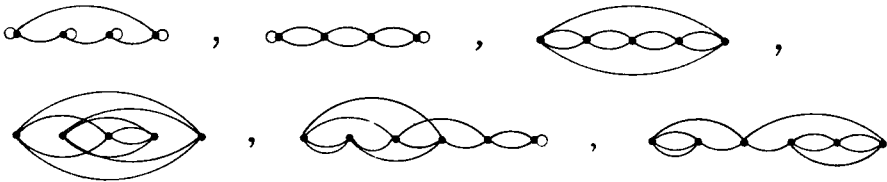


Fig. 3. Examples of diagrams belonging to  $Z_5$

from a bounded  $T$ -chain considered in ref. [5] has been found there to be  $\exp[-\beta(V+2wF)]$ , the factors  $V$  and  $wF$  proceeding from the internal contractions of the type of  $\langle aa^+ \rangle_0$  and  $\langle a^+a \rangle_0$ , respectively. However, it has been also shown there that the factor  $wF$  is proportional to the density of the gas, whereas the factor  $V$  is of zeroth order in density. Thus, as the virial expansion is equivalent to the expansion in density, we must redefine the notion of a  $T$ -chain to include the factor  $V$  only, and the factor  $wF$  will be contained directly in the  $Z_j$ 's. In fact, the first diagrams from Figs 1-3 are built up from  $T$ -interactions (of the type of  $wF$ ) only, and some other diagrams from Figs 2 and 3 also contain some  $T$ -interactions of this type directly. This type of internal linking is now denoted by the loop, i.e., by the line which begins and ends at the same point (which links a point with itself). The loop thus

replaces the final  $T$ -chain of ref. [5] and according to the above redefinitions and to the results found in [5], the contribution to a given simplified diagram from all the  $T$ -interactions contained in it (*i.e.*, the effect of dressing a diagram into  $T$ -interactions in all possible ways) will be the factor  $\exp(-j\beta V)$ , where  $j$  denotes the number of upper lines (including the loops) in the considered diagram<sup>2</sup>. The examples of such a dressing are given in Fig. 4.

$$\begin{aligned} \text{---} \circ &= \left| \begin{array}{c} || \\ +\circ +\circ \end{array} \right| + \left| \begin{array}{c} || \quad || \\ +\circ +\circ \quad +\circ +\circ \end{array} \right| + \left| \begin{array}{c} || \quad || \quad || \\ +\circ +\circ \quad +\circ +\circ \quad +\circ +\circ \end{array} \right| + \dots, \\ \text{---} \curvearrowright &= \left| \begin{array}{c} || \quad || \quad || \\ +\circ +\circ \quad +\circ +\circ \end{array} \right| + \left| \begin{array}{c} || \quad || \quad || \\ +\circ +\circ \quad +\circ +\circ \quad +\circ +\circ \end{array} \right| + \dots \end{aligned}$$

Fig. 4. Examples of presently considered  $T$ -chains

The term  $Z_1$ , containing the diagrams with one upper line, is thus composed of  $T$ -interactions only. It is easy to realize that the contribution from it is equal  $F[\exp(-\beta V)-1]$ , and, because  $\ln Z_0 = F = \sum_{\mathbf{p}} f_{\mathbf{p}}$  (*cf.* [5]), the total contribution from the first two terms of (4.3) is

$$\ln Z_0 + Z_1 = F \exp(-\beta V) = N_{id} = \langle N \rangle_0, \quad (4.4)$$

where  $N_{id}$  denotes the average number of particles as calculated for the classical system of non-interacting particles (ideal classical gas).

Let us now calculate the contribution  $Z_2$ , given graphically in Fig. 1. It is easy to find that in the Boltzmann approximation,  $f_{\mathbf{p}} \ll 1$ , and according to (4.2), the analytic expression for this series is<sup>3</sup> (compare with [5])

$$\begin{aligned} Z_2 &= \frac{1}{2} F^2 e_i^{-2\beta V} \left\{ (-\beta\lambda) 2\tilde{v}(0) + \right. \\ &+ \left. \sum_{n=2}^{\infty} \frac{(-2\beta\lambda)^n}{n!} \sum_{\mathbf{q}^1} \tilde{v}(\mathbf{q}_1) \dots \sum_{\mathbf{q}_{n-1}} \tilde{v}(\mathbf{q}_{n-1}) \tilde{v}(\mathbf{q}_1 + \dots + \mathbf{q}_{n-1}) \right\}. \end{aligned} \quad (4.5)$$

By definition,

$$\lambda \tilde{v}(\mathbf{q}) = \frac{1}{2\Omega} \int d^3r e^{i\mathbf{q} \cdot \mathbf{r}} V(\mathbf{r}), \quad (4.6)$$

where  $V(\mathbf{r})$  is the intermolecular (pairwise) potential function, and  $\Omega$  is the volume of the system. Thus, Eq. (4.5) can be written in the form (compare with (4.4)):

$$Z_2 = \frac{N_{id}^2}{\Omega} \frac{1}{2} \int d^3r [e^{-\beta V(\mathbf{r})} - 1], \quad (4.7)$$

<sup>2</sup> Note that the terms proportional to  $\sum_{\mathbf{p}} f_{\mathbf{p}}^n$ ,  $n > 1$ , are neglected in comparison with the terms proportional to  $F = \sum_{\mathbf{p}} f_{\mathbf{p}}$ , according to the assumption that classical systems,  $f_{\mathbf{p}} \ll 1$ , are considered.

<sup>3</sup> The factor 2 corresponding to every point ( $W$ -interaction) comes from two internal pairs ( $a^+a$ ), the factor 1/2 corresponding to the whole diagram — from its symmetry. We neglect here entirely the exchange terms (the second possibility of exchanges of the two  $a^+$  and two  $a$  within every interaction), as being of essentially quantum nature.

where the properties of the Fourier transform of a convolution have been applied. In order to find the dependence of (4.7) with respect to the pressure, let us remark that  $N_{id}$  is the average number of particles of the system under consideration (*i.e.*, in the same temperature  $T$ , pressure  $P$ , and volume  $\Omega$ ), but treated as an ideal gas, and thus  $N_{id}$  is to be calculated from the ideal gas laws, *i.e.*,  $(N_{id}/\Omega) = P/kT$ . Hence,

$$Z_2 = N_{id}K_1(T) \frac{P}{kT}, \quad K_1(T) = \frac{1}{2} \int d^3r [e^{-\beta V(r)} - 1]. \quad (4.8)$$

Note that  $-K_1(T)$  is nothing but the usual second virial coefficient of the virial equation of state [9, 10].

The higher-order terms,  $Z_j$ , can be evaluated in the same way. Note that  $Z_j$  will be proportional to  $(N_{id})^j/(\Omega)^{j-1} = N_{id}(P/kT)^{j-1}$ , which can be easily checked by considering any diagram containing  $j$  upper lines. Indeed, every upper line produces the factor  $F \exp(-\beta V) = N_{id}$ ; on the other hand, the Kronecker deltas appearing from the contractions (compare with (3.5)) lead to the cancellation of some momentum summations and thus, eventually, the factor  $\Omega^{-j+1}$  appears from (4.6) (for example, the first diagram in Fig. 3 is proportional to  $[\tilde{v}(0)]^4 \sim \Omega^{-4}$ ). We can thus write

$$Z_j = N_{id}K_{j-1}(T)(P/kT)^{j-1}, \quad (4.9)$$

where  $K_j(T)$  are functions of the intermolecular potential  $V(r)$  and temperature only. This gives the virial expansion of the partition function:

$$\ln Z = N_{id} \sum_{j=0}^{\infty} K_j(T) \left( \frac{P}{kT} \right)^j, \quad K_0 = 1. \quad (4.10)$$

The virial expansion of the equation of state can be obtained from (4.10) by means of the relations:

$$\ln Z = P\Omega/kT, \quad N = kT \left( \frac{\partial \ln Z}{\partial \mu'} \right)_{\beta, \Omega}, \quad (4.11)$$

where  $\mu'$  is the (unmodified) chemical potential of the system, and  $N$  is the actual (average) number of particles composing the system under consideration. In using the second of the relations (4.11), it should be remembered that the pressure  $P$  is a function of  $\mu'$  through the relation

$$\frac{P}{kT} = \frac{N_{id}}{\Omega} = \frac{1}{\Omega} \sum_{\mathbf{p}} \exp(\beta\mu' - \beta\varepsilon_{\mathbf{p}}). \quad (4.12)$$

Relations (4.11) together with (4.10) make it possible to express the functions  $K_j(T)$  (virial coefficients of the partition function) by the virial coefficients of the equation of state. The relations between these virial coefficients are listed in the Appendix. Let us remark that the virial coefficients can be evaluated by means of the standard method of Ursell and Mayer (*cf.*, *e.g.*, [9, 10]), which seems to be simpler than the method described in this Section.



5. Virial expansion of  $\langle N(\mathbf{p}) \rangle_{class}$ .

The virial expansion of the Maxwell-Boltzmann distribution  $\langle N(\mathbf{p}) \rangle$  of a real classical gas can be now easily found from the expansion (4.10), by applying the method of Section 3 (or Section 2, as well), together with the relation (4.12). The result is, simply,

$$\langle N(\mathbf{p}) \rangle = f'_p \sum_{j=0}^{\infty} (j+1) K_j(T) \left( \frac{P}{kT} \right)^j, \quad (5.1)$$

where

$$f'_p = \exp(\beta\mu' - \beta\varepsilon_p) \quad (5.2)$$

is the Maxwell-Boltzmann distribution of an ideal gas.

The above result means that the distribution of momentum between the particles of a real gas remains the same as that for an ideal gas. The only changes appear in the functional dependence of  $\langle N(\mathbf{p}) \rangle$  on the temperature and pressure of the gas. If the expansion (4.10) is valid also for the liquid phase (which, according to present knowledge, is not certain), the same conclusion will hold for the particles of a liquid. Moreover, summing (5.1) over  $\mathbf{p}$ , we find that

$$\langle N(\mathbf{p}) \rangle / N = f'_p / N_{id} = f'_p(kT/P\Omega), \quad (5.3)$$

i.e., the fraction of particles possessing the momentum  $\hbar\mathbf{p}$  (or the kinetic energy  $\varepsilon_p$ ) in a real gas (and perhaps even in a liquid) is the same as in an ideal gas under the same external conditions, if the total number of particles is calculated from the Clapeyron equation, instead of from the density.

It is noteworthy that a somewhat similar result has been recently obtained by Kupelian [11], who found that the higher random phase approximations to the Luttinger model (of two-dimensional, massless, two-component fermions) do not disturb the free-gas momentum distribution.

## APPENDIX

The virial expansion of the equation of state is [10]:

$$\frac{P\Omega}{NkT} = 1 + \sum_{n=1}^{\infty} A_n(T) P^n, \quad (A.1)$$

The quantities  $A_n$  are called the  $(n+1)$ -th virial coefficients, and can be determined experimentally as functions of temperature.

The relations between the coefficients  $K_n$  of the expansion (4.10) and (5.1) of  $\ln Z$  and  $\langle N(\mathbf{p}) \rangle$ , and the virial coefficients  $A_n$  from (A.1) are:

$$\begin{aligned} (kT)A_1 &= -K_1, & (kT)^2A_2 &= -2K_2 + 2K_1^2, \\ (kT)^3A_3 &= -3K_3 + 7K_1K_2 - 4K_1^3, \\ (kT)^4A_4 &= -4K_4 + 10K_1K_3 + 6K_2^2 - 2K_1^2K_2 + 8K_1^4, \\ (kT)^5A_5 &= -5K_5 + 13K_1K_4 + 17K_2K_3 - 28K_1^2K_3 - 33K_1K_2^2 + 70K_1^3K_2 - 16K_1^5, \\ (kT)^6A_6 &= -6K_6 + 16K_1K_5 + 22K_2K_4 - 36K_1^2K_4 + 12K_3^2 - 92K_1K_2K_3 + \\ &+ 72K_1^3K_3 - 18K_2^3 + 144K_1^2K_2^2 - 8K_1^4K_2 + 32K_1^6, \end{aligned} \quad (A.2)$$

and

$$\begin{aligned}
K_1 &= -kTA_1, & K_2 &= (kT)^2 \left( -\frac{1}{2} A_2 + A_1^2 \right), \\
K_3 &= (kT)^3 \left( -\frac{1}{3} A_3 + \frac{7}{6} A_1 A_2 - A_1^3 \right), \\
K_4 &= (kT)^4 \left( -\frac{1}{4} A_4 + \frac{5}{6} A_1 A_3 - \frac{25}{6} A_1^2 A_2 + \frac{8}{3} A_2^2 + \frac{11}{2} A_1^4 \right), \\
K_5 &= (kT)^5 \left( -\frac{1}{5} A_5 + \frac{13}{20} A_1 A_4 + \frac{17}{30} A_2 A_3 - \frac{43}{30} A_1^2 A_3 - \frac{157}{120} A_1 A_2^2 + \right. \\
&\quad \left. + \frac{311}{30} A_1^3 A_2 - \frac{163}{10} A_1^5 \right), \\
K_6 &= (kT)^6 \left( -\frac{1}{6} A_6 + \frac{8}{15} A_1 A_5 + \frac{11}{24} A_2 A_4 - \frac{23}{20} A_1^2 A_4 - \frac{367}{180} A_1 A_2 A_3 + \right. \\
&\quad \left. + \frac{73}{30} A_1^3 A_3 + \frac{2}{9} A_2^3 - \frac{325}{72} A_2^2 + \frac{269}{90} A_1^2 A_2^2 - \frac{7411}{180} A_1^4 A_2 + \frac{553}{10} A_1^6 \right). \quad (\text{A.3})
\end{aligned}$$

The expansion of the compressibility factor ( $PQ/RT$ ) into powers of density, or inverse volume, of the system is also called the virial expansion [9, 10]. The relations between the coefficients  $K_j$  and the coefficients of the above-mentioned expansions can be found by means, e.g., of the known relations between different virial coefficients [10].

## REFERENCES

- [1] R. Balian, in *Lectures on the Many-Body Problems* (E. R. Caianiello, Editor), Acad. Press, New York-London 1962, pp. 139-162. C. De Dominicis, *ibid.*, pp. 163-189.
- [2] C. Bloch, in *Studies in Statistical Mechanics* (J. de Boer, G. E. Uhlenbeck, Editors), Vol. III, North-Holland Publ. Co., Amsterdam 1965, pp. 1-211.
- [3] A. Fuliński, *Acta Phys. Polon.*, **27**, 245 (1965); **29**, 163, 205 (1966).
- [4] J. de Boer, in *Studies in Statistical Mechanics*, Vol. III, North-Holland Publ. Co., Amsterdam 1965, pp. 213-275.
- [5] A. Fuliński, *Physics Letters*, **25 A**, 585 (1967); *Acta Phys. Polon.*, **33**, 281, 291 (1968); **34**, 79, 91 (1968).
- [6] A. Fuliński, M. Zgierski, *Acta Phys. Polon.*, **34**, 119 (1968).
- [7] N. M. Hugenholtz, in *Fundamental Problems in Statistical Mechanics* (compiled by E. G. D. Cohen), North-Holland Publ. Co., Amsterdam 1962, pp. 86-109.
- [8] D. J. Thouless, *The Quantum Mechanics of Many-Body Systems*, Acad. Press. New York-London 1961, p. 139.
- [9] K. Huang, *Statistical Mechanics*, Wiley, New York-London 1963.
- [10] J. O. Hirschfelder, C. F. Curtiss, R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York 1954.
- [11] N. J. Kupelian, *Phys. Rev.*, **168**, 187 (1968).