Chapter 34
A Statistical Expression of the Activity of a Species: A Relation Between It and the Corresponding Concentration in the Case of an Imperfect Gas

Abstract This chapter brings some elements of answer to one of the most significant questions regarding the notion of activity, i.e., how are, mathematically related to each other, the value of an activity and that of the corresponding "concentration" of a species when the latter, no longer, tends toward zero? Recall, indeed, that G.N. Lewis, when he introduced it, defined the notion of activity by the following sentence:

> a quantity which is "an active density number which bears the same relation to the chemical potential μ at any density that N/V does as $N \rightarrow 0$."

The results mentioned in this chapter constitute a first mark of the fact that statistical thermodynamics permits, at least in part, to answer the question. The content of this chapter shows that the setting up of the expression relating the activity of a gas to its corresponding concentration stems from a reasoning which, at the onset, requires the definition of the activity in terms of statistical parameters. It also shows that the obtained relation involves terms which are related to the virial coefficients. According to the theory, an activity z of a compound can be identified to the product of its absolute activity λ and of the second canonical function of the grand ensemble $Q_1(N, V, T)$ (that is to say that corresponding to the presence of only one particle in the system), product divided by the volume V of the system. The relation also shows that z exhibits all the properties of Lewis' activity. It has the form of a series development of z in density ρ, the coefficients of which can be, in principle, calculated from the experimental values of the virial relation.

Keywords Statistical expression of the activity of a species • Activity–concentration relation of an imperfect gas • Lewis' definition of an activity • Statistical analogue of the activity • Configuration integral • Activity and concentration relation • Grand ensemble • Series development • Density number • Activity and virial coefficient relation • Fugacity in statistical thermodynamics • Virial coefficients and configuration integrals

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The results mentioned in this chapter constitute a first mark of the fact that statistical thermodynamics permits, at least in part, to answer the question.

We shall see that the obtaining of the expression relating the activity of a gas to its corresponding concentration stems from a reasoning which, at the onset, requires the definition of the activity in terms of statistical parameters. We shall also see that the obtained relation involve terms which are related to the virial coefficients which can be experimentally obtained.

34.1 The Followed Reasoning

Let us recall the fact that the handling of the activity coefficient (and of that of fugacity) finds all its interest when there are interactions between the particles constituting the system. We know indeed (viz. Chap. 32) that, that in the framework of the "pairwise additivity" hypothesis, the expression of the chemical potential of the component is:

$$\mu = \mu^{0\mathrm{g}} + kT\ln\rho - kT\ln\langle\exp(-B/kT)\rangle$$

It contains the term $-kT\ln\langle\exp(-B/kT)\rangle$ which takes into account the interactions between the particles.

The reasoning followed in order to obtain the relation being searched for consists in:

- In a first step, arbitrarily defining a parameter z which exhibits the behavior of the activity as it has been introduced by Lewis, i.e., that $z \rightarrow \rho$ when $\rho \rightarrow 0$. We can call this quantity *the statistical analog* of the activity, symbolized by z.
- In a second one, setting up the mathematical relation activity–concentration being searched for. It requires the crossing through the configuration integrals Z_N.
- In a third step, then, to set up the relations between the parameters playing a part in the preceding relations and the virial coefficients applying to the real gases (for which, actually, there exist interactions between the different particles).

At this point of the reasoning, we justify the calculations and the validity of the statistical definition adopted for the activity. Then, we demonstrate that one of the parameters involved in the preceding calculations is actually equal to a configuration integral. Then, we shall perform a brief analysis of the physical meaning of the activity of a gas and give a statistical definition of its fugacity. Finally, we shall give the expression of the virial coefficients as a function of the configuration integrals.

34.2 Introduction of the Activity

Let us consider a mono or polyatomic gas. Let us reason within the framework of the grand ensemble. We know that the partition function can be written (viz. Chap. 24):

$$\Xi(\lambda, V, T) = \mathrm{e}^{pV/kT} \tag{34.1}$$

the term **p**V/kT representing the thermodynamic function characteristic of the grand ensemble (viz. Appendix V). We also know that (viz. relation (33.9)—previous chapter):

$$\Xi(\lambda, V, T) \;=\; 1 + \sum_{N \geq 1} Q_N(V, T)\lambda^N \tag{34.2}$$

where

$$Q_N(V, T) = Q(N, V, T) \quad \text{and} \quad \lambda = \mathrm{e}^{\mu/kT}$$

$Q_N(V, T)$ is the canonical partition function entailing the constant number N of particles which, with other canonical functions taking into account different numbers, enters into the grand canonical partition function. Equation (34.2) is the expansion in series of Ξ in λ. The parameter λ has already been introduced and is, in the occurrence, called the absolute activity of the gas (viz. Chap. 24).

According to what is preceding:

$$\mathbf{p}V/kT = \ln\left[1 + \sum_{N \geq 1} Q_N(V, T)\lambda^N\right] \tag{34.3}$$

Let us develop the logarithm in series. By only retaining the first terms, we obtain:

$$\ln\left[1 + \sum_{N \geq 1} Q_N\lambda^N\right] = \left[Q_1\lambda + Q_2\lambda^2 + Q_3\lambda^3 + \cdots\right] - \left[Q_1\lambda + Q_2\lambda^2 + Q_3\lambda^3 + \cdots\right]^2/2 + \ldots \tag{34.4}$$

i.e.:

$$\ln\left[1+\sum_{N\geq 1} Q_N\lambda^N\right] \approx Q_1\lambda \tag{34.5}$$

according to the relation:

$$\ln(1+x) = x - 1/2x^2 + 1/3x^3 - 1/4x^4 + \cdots \quad (-1 < x \leq 1)$$

$$\ln\Xi \approx Q_1\lambda \tag{34.6}$$

The equivalent expressions (34.5) and (34.6) induce the introduction of the parameter z defined by the following expression:

$$z = Q_1\lambda/V \tag{34.7}$$

The interest to adopt this definition is to show that, actually:

$$z \rightarrow \rho \quad \text{when} \quad \rho \rightarrow 0$$

The property of z to tend toward ρ is only true if all the other terms of the development are lower than that kept.

As we shall see below, z exhibits the properties of Lewis' activity. z is called *a statistical analogue of the activity*.[1] With this choice, according to relation (34.1) we can write:

$$PV/kT = Q_1\lambda \tag{34.8}$$

A beginning of proof of the identity of the Lewis' activity and of z is provided by demonstrating that $z \rightarrow \rho$ when $\rho \rightarrow 0$ which, indeed, is the definition of Lewis, originating in thermodynamics.

The identification of z to the Lewis' activity firstly entails to set up a relation between the density number ρ and z. We immediately do that in two steps. In the first step, we show that z tends toward ρ when the latter tends toward zero. In the second step, we set up the relation being searched for.

34.3 Analogy of the Behaviors of z and of ρ When ρ Tends Toward Zero

Since we are reasoning by using the grand ensemble, the density number is given by the relation:

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[1] Within the framework of statistical thermodynamics, we use the symbol z instead of a in order to mark the fact than z is introduced by the statistical way.

$$\rho = \overline{N}/V \tag{34.9}$$

The number of particles cannot be anything else than an average number given the use of the grand ensemble. We have seen (viz. Chap. 33) that:

$$\overline{N} = \lambda(\partial \ln \Xi/\partial \lambda)_{V,T} \tag{34.10}$$

According to (34.9) and (34.10), the condition:

$$\rho \rightarrow 0$$

entails that:

$$\overline{N} \rightarrow 0 \quad \text{and} \quad \lambda \rightarrow 0$$

According to the statistical definition of the activity (adopted above), the relation (34.7) is evidently satisfied lorsque $\lambda \rightarrow 0$, $z \rightarrow 0$. Consequently:

$$z \rightarrow \rho \quad \text{when} \quad \rho \rightarrow 0$$

The quantity $z = Q_1\lambda/V$, from purely statistical origin, exhibits the same behavior as the Lewis activity, at least when $\rho \rightarrow 0$.

34.4 Relation Between the Number of Density ρ and Activity z

We have seen that, within the framework of the hypothesis of the truncation of the series development of the grand partition function Ξ as a function of λ, the activity z tends toward the density number of the gas ρ when the latter tends toward zero. It is no longer the case when the latter does not tend toward zero.

Now, we set up a more general relation between z and ρ than that constituting the Lewis' definition.

Let us replace λ by z into (34.3) through:

$$\lambda = zV/Q_1$$

We obtain:

$$\Xi = 1 + \sum_{N \geq 1} \left(Q_N V^N/Q_1^N\right) z^N \tag{34.11}$$

Let us introduce the term Z_N by the relation:

$$Z'_N = N!\left[Q_N/Q_1^N\right]V^N \tag{34.12}$$

As we have already mentioned it in Chap. 28 and as we demonstrate it (viz. paragraph 8), Z_N is nothing else than the configuration integral $Z_{N.}$ Expression (34.11) can be, now, written by already assimilating Z'_N to Z_N. Therefore:

$$\Xi = 1 + \sum_{N\geq 1} (Z_N/N!)z^N \tag{34.13}$$

Let us take the logarithm of both members of this equality, i.e.:

$$\ln\Xi = \ln\left[1 + \sum_{N\geq 1} (Z_N/N\,!)\, z^N\right] \tag{34.14}$$

or, taking into account (34.1):

$$pV/kT = \ln\left[1 + \sum_{N\geq 1} (Z_N/N!)\, z^N\right] \tag{34.15}$$

Let us divide the above equation by V and expand in series the logarithm. We can easily forecast that we shall obtain one relation of the type:

$$p/kT = b_1 z^1 + b_2 z^2 + b_3 z^3 + \cdots \tag{34.16}$$

or equivalently:

$$p/kT = \sum_{j\geq 1} b_j z^j \tag{34.17}$$

Or

$$pV/kT = V\sum_{j\geq 1} b_j z^j \tag{34.18}$$

or

$$\ln\Xi = V\sum_{j\geq 1} b_j z^j \tag{34.19}$$

$b_1, b_{2,}$ …. depend on temperature owing to the fact that we are reasoning within the framework of the great ensemble.

The simple fact to identify the terms of same degree in z of both members of relation (34.19), after having expanded in series the logarithm of the kind ln $(1 + x)$

of relation (34.15) by using the symbol $x = \sum\limits_{N \geq 1} (Z_N/N!)\, z^N$, permits to immediately find:

$$\begin{gathered} Vb_1 \equiv Z_1 \quad \text{i.e.} \quad b_1 = 1 \\ Vb_2 \equiv \left(Z_2 - Z_1^2\right)/2 \\ Vb_3 \equiv \left(Z_3 - 3Z_1Z_2 + Z_1^2\right)/3! \\ \vdots \end{gathered} \tag{34.20}$$

Hence, coefficients b_1, b_2, b_3... can be expressed as a function of the configuration integrals. By limiting ourselves to the term of order 3, we obtain:

$$\begin{aligned} p/kT = {} & [(Z_1/V)]z^1 + \left[(1/2V)\left(Z_2 - \ Z_1^2\right)\right]z^2 \\ & + \left[(1/6V)\left(\left(Z_3 - 3Z_1Z_2 + 2Z_1^3\right)z^3 + \cdots\right.\right. \end{aligned} \tag{34.21}$$

At this point of the reasoning, we notice that the function p/kT, which is a remnant of the perfect gas law, can be written under a series development as a function of the statistical analogue z of the activity.

The relation being searched for between ρ, z, and the coefficients b_i is found as it follows. According to (34.10):

$$\overline{N} = \lambda(\partial \ln \Xi/\partial \lambda)_{V,T} \tag{34.22}$$

Since:

$$\lambda = (V/Q_1)z$$

i.e.:

$$d\lambda = (V/Q_1)dz$$

As a result:

$$\overline{N} = z(\partial \ln \Xi/\partial z)_{V,T}$$

According to (34.1),

$$\begin{gathered} \overline{N} = z[\partial(pV/kT)/\partial z]_{V,T} \\ \overline{N}/V = \rho = z[\partial(p/kT)/\partial z]_T \end{gathered} \tag{34.23}$$

and according to (34.17):

$$\begin{aligned}[\partial(p/kT)/\partial z]_T &= \sum_{j\geq 1} jb_j(T)z^{j-1} \\ \rho &= \sum_{j\geq 1} jb_j(T)z^j\end{aligned} \tag{34.24}$$

The relation (34.24) between the density number ρ and the activity of the component z is that which is being searched for. It depends on the configuration integrals Z_N, parameters stemming from statistical thermodynamics through the coefficients b_j.

Another interesting relation is its reciprocal one, i.e., that relating the activity z to the density number ρ. Let us assume that it is of the following analytical type:

$$z = a_1\rho + a_2\rho^2 + a_3\rho^3 + \cdots \tag{34.25}$$

At once, one can remark that a_1 is set up equal to 1 in agreement with what is preceding. In order to find the other coefficients a_n, it is sufficient to replace z by its development (34.25) into its expression (34.24) and to identify the terms of the same degree in ρ. Hence, by limiting ourselves to the terms of degree 2, we obtain:

$$\begin{aligned}\rho &= b_1(\rho + a_2\rho^2) + 2b_2(\rho + a_2\rho^2)^2 + \cdots \\ \rho &= b_1\rho + b_1a_2\rho^2 + 2b_2\left(\rho^2 + 2a_2\rho^3 + a_2^2\rho^4\right) + \cdots \\ \rho &= b_1\rho + (b_1a_2 + 2b_2)\rho^2 + \text{terms of superior degrees}\end{aligned}$$

We deduce that, since $b_1 = 1$, the terms of superior degrees must be null, i.e.,

$$a_2 = -2b_2$$

Likewise, we would find:

$$\begin{aligned}a_3 &= -3b_3 - 4a_2b_2 \\ a_3 &= -3b_3 + 8b_2^2 \text{ etc}\ldots\end{aligned}$$

Such is the relation (34.25) between the activity z and the density number, whatever the value of the latter is. Its coefficients a_1, a_2 … are accessible by starting from experimental data. Actually, from the practical standpoint, it is more interesting than the relation (34.24). The density numbers being, indeed, data which are immediately at our disposal, it is possible to reach the value of the activity which is a thermodynamic data very important, as we have already said it. In principle, the calculation can be done whatever the value of ρ is.

34.5 Discussion Around the Relation Between the Activity and the Corresponding Concentration of the Imperfect Gas

The relation (34.25) is at the core of our purpose. It can also be written:

$$z = \rho - 2b_2\rho^2 + \left(-3b_3 + 8b_2^2\right)\rho^3 + \cdots \tag{34.25}$$

with the coefficients b_2, b_3, ... which are function of the configuration integrals and which are related to the virial coefficients (viz. the following paragraph).

We notice that:

- When ρ tends toward zero, z tends toward ρ
- z varies with ρ
- According to the Lewis' definition of the activity, for every "concentration" ρ, the chemical potential of the species must obey the relation:

$$\mu = \mu_0 + RT\ln z$$

As a result, z appears as being a *pseudo-concentration* which would confer the same value to the chemical potential of the species as actually its concentration ρ does, whatever its value, *during an ideal behavior*.

Unfortunately, in our current state of calculations, the expression (34.25) cannot be anything else than a formal one, although as a rule, it permits the calculation of the activity for every "concentration," provided the values of the virial coefficients are known after experimental measurements. The number of the virial coefficients to know may be huge, owing to the recurrence of the calculation of the coefficients b_i and a_i (about 10^{20} coefficients!).

34.6 Relations Between the Density Number of the Gas, Its Activity, and the Virial Coefficients

It is possible to obtain the numerical values of the coefficients b_j and a_n from those of the virial coefficients which are the experimental ones. Let us, indeed, compare the virial relation:

$$p/kT = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \cdots$$

and

$$p/kT = b_1 z^1 + b_2 z^2 + b_3 z^3 + \cdots \tag{34.16}$$

Let us replace the activities z by the development (34.25) into (34.16). We obtain by writing only until the term of degree 2:

$$p/kT = b_1\left(\rho + a_2\rho^2\right) + b_2\left(\rho + a_2\rho^2\right)^2 + \cdots$$

whence:

$$p/kT = b_1\rho + (a_2 b_1 + b_2)\rho^2 + \cdots \tag{34.26}$$

By comparing (34.26) and the virial relation and by taking into account the a_n expressions as a function of b_j previously obtained, we find:

$$\begin{aligned} &B_2(T) = -b_2 \\ &B_3(T) = 4b_2^2 - 2b_3 \\ &\vdots \end{aligned}$$

Therefore, the coefficients b_j and a_n (the latter ones through the reciprocal relation) can be expressed as a function of the virial coefficients.

Moreover, it appears that the coefficients a_n do not depend on the coefficients b_j when $j > n$. For example, a_2 only depends on b_2 and on b_1, i.e., only on the configuration integrals Z_1 and Z_2. It is the same thing for a_n and b_n which only depend on the configuration integrals $Z_1 \ldots Z_n$. This point is very important. It means that these coefficients together with those of the virial, take into account:

- When b_2, a_2, $B_2(T)$ are concerned, only the interactions between two particles
- When b_3, a_3, $B_3(T)$ are concerned, only the interactions between three particles
- When b_n, a_n, $B_n(T)$ are concerned, only those between n particles.

In other words, $B_2(T)$ only depends on the interactions between two particles, etc.

34.7 Justification of the Preceding Calculations. Validity of the Statistical Definition of the Activity

The problem, now, is to justify the validity of relation (34.16).

A first point to notice before the justification is the characteristic of the reasoning followed up to now. It is the embedding and the interdependence of the different calculations. Consequently, if the legitimacy of expression (34.19) can be demonstrated, all the inferences stemming from it become legitimate.

From the pure mathematical standpoint, the difficulty lays in the fact that, at this point of the reasoning, it is not sure at all that the expansion in series, stemming from (34.15), can be truncated as it has been done.

The justificatory reasoning given below can be qualified of “upside down reasoning.” We start from the expression (34.16) set up, postulated as being a priori perfectly legitimate, and we demonstrate that we come back to expression (34.15).

According to (34.16), we have:

$$\mathrm{e}^{pV/kT} = \exp\left[V\sum_{j\geq 1} b_j z^j\right]$$

Because of the properties of the exponential function:

$$\exp\left[V\sum_{j\geq 1} b_j z^j\right] = \exp\left(Vb_1z^1\right)\cdot\exp\left(Vb_2z^2\right)\cdot\exp\left(Vb_3z^3\right)\cdots \tag{34.27}$$

Let us develop in series the exponentials of the right member of this expression and let us perform the products. Let us explicit the product of the two series developments (limited to the third degree) of the first two exponentials. This product is:

$$\begin{aligned}\exp(Vb_1z^1)\cdot\exp(Vb_2z^2) = {} & \left[1+(Vb_1)^1z^{11}+1/2!(Vb_1)^2z^{12}\right.\\ & \left.+\,1/3!(Vb_1)^3z^{13}+\cdots\right]\\ \bullet\ & \left[1+(Vb_2)^1z^{21}+1/2!(Vb_2)^2z^{22}+1/3!(Vb_2)^3z^{23}+\cdots\right]\end{aligned}$$

(Notice the use of both indices qualifying the activities, the first one permitting the mark of the coefficient $b_{j,}$ the second being the exponent). The calculation performed by multiplying the previous product by the series development of the third exponential $\exp(Vb_3z^3)$ leads to a series development as a function of z the coefficients of the increasing powers of which are:

$$\begin{array}{lll} \text{for}\quad z^1 & z^2 & (Vb_1/1)\\ \text{for}\quad z^2 & z^2 & \tfrac{1}{2}(Vb_1)^2+(Vb_2/1)\\ \text{for}\quad z^3 & z^3 & 1/3!(Vb_1)^3+(Vb/1)(Vb_2/1)+(Vb_3/1)\\ \vdots & & \end{array}$$

Equalizing the coefficients Z_N of equation (34.13) and those of equation (34.27), we obtain the equalities:

$$(Vb_1/1) = Z_1$$

$$½(Vb_1)^2 + (Vb_2/1) = 1/2Z_2$$

$$1/3!(Vb_1)^3 + (Vb_1/1)(Vb_2/1) + (Vb_3/1) = 1/6Z_3$$

In brief, we again find expression (34.13). It is the result that we wanted to demonstrate.

34.8 Identity of Z'_N and of the Integral of Configuration in Classical Statistical Thermodynamics Z_N

We have already mentioned in the paragraph 4 that the parameter Z'_N introduced in the preceding calculations and defined by the expression:

$$Z'_N(V,T) = N!\left[Q_N/Q1^N\right]V^N \tag{34.12}$$

is identical to the corresponding configuration integral Z_N in classical statistical thermodynamics, defined by the expression (viz. Chap. 28):

$$Q_{\text{class}} = Z_N/N\,!\Lambda^{3N} \tag{34.28}$$

Hence, we must demonstrate that:

$$Z'_N \equiv Z_N$$

When the gas is very weakly concentrated, it exhibits a perfect behavior. It is obviously the case when there is only one molecule in the system, to which corresponds the partition function Q_1 by definition. Since the gas behaves ideally, the following expression is justified (viz. Chap. 26):

$$Q = (1/N!)q^N$$

and therefore for $N = 1$:

with:

$$q = V/\Lambda^3$$

where q is the molecular partition function of the system—viz. Chap. 27. As a result:

$$Q_1 \ = V/\Lambda^3$$

Replacing Q_1 into (34.12) by the latter expression immediately leads to the identity being searched for.

34.9 Physical Meaning of the Activity of a Gas

In this paragraph, we briefly comment on the results which we have obtained just above.

- Let us begin by saying that relations (34.24) and (34.25) show distinctly how the activity and the density numbers differ from each other. The relation (34.25), for example, shows that the difference between both is expressed by terms containing the density number itself at degrees larger than 2. As a result, one can conceive that the more dense the gas is, the larger the difference between both quantities may be. This conclusion can also be found when the notion of activity coefficient is regarded (viz. Chap. 37).
- Let us consider the relation (34.7) defining the activity:

$$z = Q_1\lambda/V \tag{34.7}$$

Clearly, the activity takes its roots in classical thermodynamics through the absolute activity λ. Certainly, the absolute activity is a quantity which is introduced in statistical thermodynamics at the level of the grand ensemble, but its definition:

$$\lambda = \mathrm{e}^{\mu/kT}$$

involves the concept of chemical potential of purely thermodynamic origin. Clearly, we notice that, by its sole definition, the activity of a substance is linked to its chemical potential.

- Still more significant than the last argument is the occurrence of the canonical partition function Q_1 in the definition of the activity. It is a characteristic of the system which possesses one particle only in the system V. No interaction with other particles, of course, can exist. Here, we again find the meaning which was attributed to an activity by Lewis himself: i.e., to characterize a species as it would have no interaction with other ones. (In passing let us recall that, according to the general principles of quantum mechanics, Q_1 depends on the volume V and on the fact that there is one molecule in the system).

34.10 Definition of the Fugacity

Incidentally, in this paragraph, we are interested in the meaning of the fugacity in statistical thermodynamics. According to Lewis, the fugacity is defined as being the quantity which tends toward the pressure p of a gas when the latter tends toward zero (viz. Chap. 7), i.e.,

$$\lim_{p \to 0} f = p$$

According to relation (34.24), it is evident that:

$$p/kT \to b_1 z^1 \quad \text{when} \quad p \to 0$$

Since $b_1 = 1$, and since $f \to p$ when $p \to 0, f$ must be defined by the expression:

$$f = kTz \quad f/kT = z \tag{34.29}$$

i.e.,

$$f = (kT/V)Q_1\lambda \tag{34.30}$$

34.11 Virial Coefficients and Configuration Integrals

We have mentioned in the preceding chapter that the virial coefficient of order 2, $B_2(T)$ can be expressed as a function of the configuration integrals Z_2 and Z_1.

$$B_2(T) = -(1/2V)\left(Z_2 - Z_1^2\right)$$

It can also be written according to:

$$B_2(T) = -(1/2V)\left\{\int_V\int \exp[-U(\mathbf{r}_1, \mathbf{r}_2)/kT] d\mathbf{r}_1 d\mathbf{r}_2 \ - V^2\right\}$$

where $U(\mathbf{r}_1, \mathbf{r}_2)$ is the intermolecular potential energy between the two particles of the system of coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ $(x_1 \ldots z_2)$. It can also be written:

$$B_2(T) \ = \ - \ (1/2) \int_0^\infty \exp[-U(r)/kT \ - \ 1] 4\pi r^2 dr$$

In the latter expression, r is a scalar. It is the distance which separates particles 1 and 2, particle 1 being supposed fixed.

Let us recall that in this special case, the configuration integral is given by the following expression:

$$Z_N = \int_V \cdots \int \exp[-U_N(x_1, \ldots z_N)/kT] dr_1 \cdots dr_N$$
$$\text{with} \quad d\mathbf{r}_1 = dx_1 dy_1 dz_1 \cdots$$

- For the calculation of Z_1, evidently $U(x_1, \ldots z_N) = 0$, since there is only one particle. Consequently:

$$Z_1 = \int_V d\mathbf{r}_1$$
$$Z_1 = V$$

- Z_2 is given by the expression:

$$Z_2 = \int_V \int \exp[-U(\mathbf{r}_1, \mathbf{r}_2)/kT] d\mathbf{r}_1 d\mathbf{r}_2$$

$U(\mathbf{r}_1,\ \mathbf{r}_2)$ is the intermolecular potential energy between the two particles, depending on the coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ ($x_1 \ldots z_2$). In order to relate $B_2(T)$ to the intermolecular potential energy between both particles, we use the equalities, already demonstrated above, in which the configuration integrals intervene:

$$B_2(T) \;=\; -b_2$$

and

$$Vb_2 \;=\; Z_2 - Z_1^2$$

whence:

$$B_2(T) = -(1/2V)\left(Z_2 - {Z_1}^2\right)$$

$$B_2(T) = -(1/2V)\left[\int_V \int \exp[-U(\mathbf{r}_1, \mathbf{r}_2)/kT] d\mathbf{r}_1 d\mathbf{r}_2 - V^2\right]$$

$$B_2(T) = -(1/2V)\int_V \int \exp[-U(\mathbf{r}_1, \mathbf{r}_2)/kT] d\mathbf{r}_1 d\mathbf{r}_2 + V/2$$

$$B_2(T) = -(1/2V)\int_V \int \exp[-U(\mathbf{r}_1, \mathbf{r}_2)/kT] d\mathbf{r}_1 d\mathbf{r}_2 + 1/2 \int d\mathbf{r}_1$$

$$B_2(T) = -(1/2V)\int_V \int \exp[-U(\mathbf{r}_1, \mathbf{r}_2)/kT] d\mathbf{r}_1 d\mathbf{r}_2 + 1/2V \int d\mathbf{r}_1 \int d\mathbf{r}_2$$

$$B_2(T) = -(1/2V)\int_V \int \exp[-U(\mathbf{r}_{1v}, \mathbf{r}_2)/kT - 1] d\mathbf{r}_1 d\mathbf{r}_2$$

By changing the variables, i.e., by using the variables d$\mathbf{r}_1$ and $\mathbf{r}_{12}=\mathbf{r}_2-\mathbf{r}_1$ (which is the location of particle 2 with respect to particle 1 regarded as being at the origin), we obtain:

$$B_2(T) \;= -(1/2V)\int_V\int \exp[-U(\mathbf{r}_{12})/kT - 1]d\mathbf{r}_{12}$$

and adopting the polar coordinates:

$$\begin{aligned} d\mathbf{r}_{12} &= 4\pi r^2 dr \\ B_2(T) &= -(1/2)\int_0^\infty \exp[-U(r)/kT - 1]\; 4\pi r^2 dr \end{aligned}$$

or, according to what is preceding:

$$B_2(T) = -1/2\int (x_{12}-1)dr_{12}$$

- By supposing the hypothesis of the “pairwise additivity” validated (besides, it is only at this term that it can be applied for the first time), the configuration integral Z_3 can be written:

$$Z_3 = \iiint_V \exp[-U(\mathbf{r}_1,\mathbf{r}_2) - U(\mathbf{r}_1,\mathbf{r}_3) - U(\mathbf{r}_2,\mathbf{r}_3)]d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3$$

By adopting a reasoning analogous to the preceding and by using the same symbolism, we obtain the following relation for $B_3(T)$:

$$B_3(T) = -(1/3V)\iiint_V v(x_{12}-1)(x_{13}-1)(x_{23}-1)d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3$$

Analogous expressions would be found for the superior coefficients.