# Chapter 32
# The Chemical Potential and the Radial Distribution Function: General Formal Introduction of the Activity and of the Activity Coefficient

**Abstract** The chemical potential $\mu$ plays a central part in the realms of physics, chemistry, and even biochemistry. It is related to the activity a of the species that it characterizes through a mathematical logarithmic relation. The latter can be formally written under only one kind of mathematical expression, whichever the type of activity is considered.

It is a well-known fact that, while relating the chemical potential of a perfect gas to molecular parameters to its number density is not endowed with any problem, it is not the case as soon as there exist interactions between the particles. In this case, the problem becomes, even, immensely complicated to solve exactly. This chapter mentions the setting up of general, but approximate, expressions, of the chemical potential of the components of a system, when such interactions exist. The first one links a decreasing exponential of the studied chemical potential to the difference of two other exponentials involving Helmholtz' energies of the system. It is obtained within the framework of the canonical ensemble. The second relation is obtained from the previous one through the using of the pairwise additivity hypothesis. It is very interesting since it takes the form of the relation expressing the chemical potential of a perfect gas, but does possess a supplementary term. The latter only takes into account the mutual interactions of the particles and, hence, must be related to an activity coefficient. Finally, the chapter also mentions the setting up of theoretical relations between the chemical potential and the radial distribution function.

**Keywords** Radial distribution function • Activity (general formal introduction) • Activity coefficient • Chemical potential (formal expression when interactions occur) • Helmholtz energy change • Chemical potential (formal expression within the framework of the pairwise additivity hypothesis) • Other general expression of the activity coefficient

The chemical potential $\mu$ plays a central part in the realms of physics, chemistry, and even biochemistry. We also know (viz. Chap. 6) that it is related to the activity a of the species that it characterizes through a mathematical logarithmic relation. We also know that the latter can be formally written under only one kind of expression, whichever the type of activity is considered.

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It is a well-known fact that, while relating the chemical potential of a perfect gas to molecular parameters to its number density is not endowed with any problem, it is not the case as soon as there exist interactions between the particles. In this case, the problem becomes, even, immensely complicated. In this chapter, we give a general expression of the chemical potential of the components of a system, when such interactions exist. We also establish theoretical relations between the chemical potential and the radial distribution function. The latter is experimentally accessible.

## 32.1 General Relations

We know with the aid of statistical theory that, in the framework of the canonical ensemble for instance, the chemical potential $\mu$ of a species is given by the relation (viz. Chap. 23):

$$\mu = -kT(\partial \ln Q/\partial N)_{T,V} \tag{32.1}$$

The canonical partition function $Q$ is given by the relation (viz. Chap. 27)

$$Q(N,T,V) = \left[q^N/\left(8\pi^2\right)^N \Lambda^{3N} N!\right)\Big] \int_{-\infty}^{+\infty} .. \int \exp\left[-\beta H\left(\mathbf{X}^N\right)\right] d\mathbf{X}^N d\mathbf{p}^N \tag{32.2}$$

with

$$\beta = 1/kT$$

Hamilton's function $H$ of the system is given by the expression:

$$H = \sum \left(\mathbf{p}_i^2, \mathbf{X}^N\right) + U_N\left(\mathbf{X}^N\right) \quad i = 1\ldots N$$

The occurrence of the symbol X is the mark that, here, we are considering the case in which the component does possess an internal structure (with the occurrence of the quantity $q \neq 1$). When this is not the case, the canonical partition function is:

$$Q(N,T,V) = \left[1/\left(N!\Lambda^{3N}\right)\right] \int_{-\infty}^{+\infty} .. \int \exp[-H/kT]\, d\mathbf{R}^N d\mathbf{p}^N \tag{32.3}$$

with

$$\begin{gathered} H = H\left(\mathbf{p}^N, \mathbf{R}^N\right) \\ H\left(\mathbf{p}^N, \mathbf{R}^N\right) = \sum \left(\mathbf{p}_i^2/2m\right) + U_N\left(\mathbf{R}^N\right) \quad i = 1\ldots N \end{gathered} \tag{32.4}$$

## 32.2 The Case of a Perfect Gas

The gas being perfect, there is by definition the lack of any intermolecular force between the particles, whence in (32.2)::

$$\mathrm{U}_N\left(\mathbf{X}^N\right)=0$$

Then, (32.2) becomes:

$$Q(N,T,V)=\left[q^N/\left(8\pi^2\right)^N\Lambda^{3\mathrm{N}}N!\right)\Big]\int_{-\infty}^{+\infty}..\int dX^N$$

or (viz.: Chap. 27):

$$Q(N,T,V)=q^N/\left(8\pi^2\right)^N\Lambda^{3N}N!\Big)\left[\int_v d\mathbf{R}\int_0^{2\pi}d\phi\int_0^{\pi}\sin\theta\, d\theta\int_0^{2\pi}d\psi\right]^N$$

that is to say

$$Q(N,T,V)=q^N V^N/\Lambda^{3N}N! \tag{32.5}$$

If the particles are simple and spherical ($q=1$), the canonical partition function reduces to:

$$Q(N,T,V)=V^N/\Lambda^{3N}N! \tag{32.6}$$

Applying relation (32.1) to (32.5) leads to (32.7) after derivation and use of Stirling's approximation:

$$\mu=kT\ln\left(\Lambda^3q^{-1}\right)+kT\ln\rho \tag{32.7}$$

where $\rho=N/V$ is the number density (more simpler the density) of the gas ($\mathrm{m}^{-3}$). It is a kind of "concentration" of the gas. Relation (32.7) can also be written:

$$\mu=\mu^{\circ\mathrm{g}}(T)+kT\ln\rho \tag{32.8}$$

$\mu^{\circ\mathrm{g}}(T)$ is, by definition, the standard chemical potential of the particle in the gaseous state. The factor $kT\ln(\Lambda^3q^{-1})$, quite evidently, takes molecular characteristics of the gas into account.

From the standpoint of the scientific accuracy, it is very satisfying to find the usual expression of the chemical potential of a gas, again. This is an argument in favor of the hypothesis constituting a basis of statistical thermodynamics, even if it is an indirect one.

*Let us notice in passing, without considering this point further, that relations (32.7) and (32.8) written as they stand, are not fully satisfactory since, in them, intervene logarithms of dimensional quantities.*

(It may seem curious to express the chemical potential of a species in a liquid phase as a function of its standard chemical potential in the gaseous phase. This must not be the case because of the fact the choice of that state is purely arbitrary, as we have already seen that. Moreover, at equilibrium, the chemical potential of the solute is the same in both phases. Hence, the choice of the standard state does not matter, but, then, activity values differ according to it).

## 32.3 A General Formal Expression of the Chemical Potential When There Exist Interactions Between the Particles of the System

Let us assume that the particles constituting the system are simple. That is to say, their configuration is only defined by the vector **R** (monoatomic particles without internal structure, $q = 1$).

In the $N$, $T$, $V$ ensemble, the chemical potential is defined by the relation (viz. Chap. 23)

$$\mu = (\partial A / \partial N)_{T,V} \tag{32.9}$$

where $A$ is the Helmholtz energy. We can also write:

$$\mu = A(T, V, N + 1) - A(T, V, N) \tag{32.10}$$

or:

$$\mu / kT = [A(T, V, N + 1) - A(T, V, N)] / kT$$

The chemical potential, indeed, is equal to the change in the Helmholtz energy $dA$ when an infinitesimal amount $dn$ mole of the species $M$ is added, at constant temperature and pressure, to the system already containing a finite amount of $M$ itself and of solvent. A "thought" equivalent process is to add 1 molecule $M$ to a very great amount of this solution. This is true because $A$ is an extensive quantity (Fig. 32.1).

Obtaining the general formal expression of the chemical potential when there are interactions between the particles is as follows. According to what is aforementioned, the change in the Helmholtz energy due to the addition of one particle to the system (in very great quantity) must be firstly expressed. Starting from (32.9) and (32.10), we obtain:

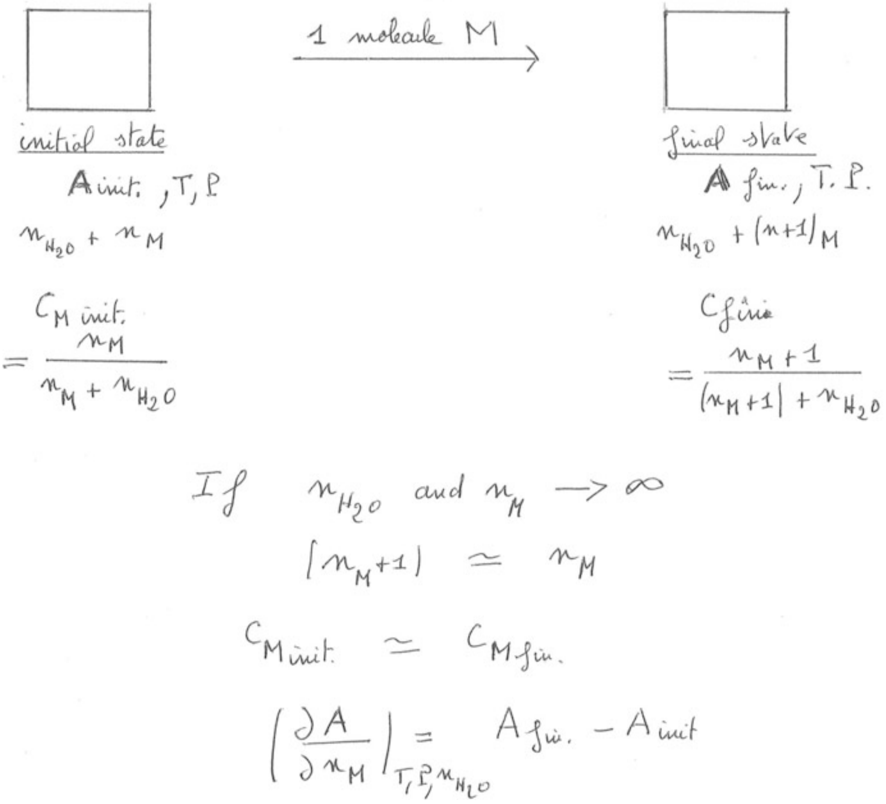

**Fig. 32.1** One way to define to define the chemical potential

$$\exp\left(-\mu/kT\right)=\exp\{-[A(T,V,N+1)-A(T,V,N)](1/kT)\}$$

Handling the general relation, characteristic of the canonical ensemble (viz. Chap. 23):

$$A(T,V,N)=-kT\ln Q(T,V,N)$$

we obtain, according to relation (32.5):

$$\begin{aligned}\exp\left(-\mu/kT\right)= \quad & \left[q^{N+1}/\Lambda^{3(N+1)}(N+1)!\right]\int v\ldots\int\exp(-\beta U_{N+1})\\ & \times d\mathbf{R}_0\ldots d\mathbf{R}_\mathrm{N}/q^N/\Lambda^{3N}N!\int v\ldots\int\exp(-\beta U_N)d\mathbf{R}_1\ldots d\mathbf{R}_N\end{aligned} \tag{32.11}$$

In the following sentences, the subscript 0 is the label of the added particle.

The general formal expression of the chemical potential when there exist interactions between particles is obtained as it follows. According to what is previously said, we must calculate the Helmholtz energy change when one molecule is added to the system. Starting from relations (32.9) and (32.10), we obtain:

$$\exp\left(-\mu/kT\right) = \exp\{-[A(T,V,N+1) - A(T,V,N)](1/kT)\}$$

This relation expresses the chemical potential of the species in the conditions of the canonical ensemble ($N$, $T$, $V$) for the kind of investigated particle. Quite evidently, it takes into account the total potential energies $\mathrm{U}_N(\mathbf{R}^N)$ and $\mathrm{U}_{N+1}(\mathbf{R}^{N+1})$ for the configurations $\mathbf{R}^N$ and $\mathbf{R}^{N+1}$.

Relation (32.11) is the expression being searched for of the chemical potential. It is general but formal. It turns out to be of great usefulness for the study of the concept of activity coefficient. This study is valid for every fluid.

## 32.4 A General Expression of the Chemical Potential in the Framework of the "Pairwise Additivity" Hypothesis

Another expression of the chemical potential can be obtained from relation (32.11) by using the "pairwise additivity" hypothesis. It consists in setting up the equality:

$$\begin{aligned} U_{N+1}(\mathbf{R}_\mathrm{o}\dots\mathbf{R}_N) &= U_N(\mathbf{R}_1\dots\mathbf{R}_N) \\ &\quad + \sum_j U\left(\mathbf{R}_\mathrm{o},\mathbf{R}_j\right) = U_N(\mathbf{R}_1\dots\mathbf{R}_N) + B(\mathbf{R}_\mathrm{o}\dots\mathbf{R}_N) \quad j = 1\dots N \end{aligned} \tag{32.12}$$

$\mathrm{U}_N(\mathbf{R}_1\dots\mathbf{R}_N)$ is the sum of potential energies, the origins of which are the interactions between particles 1 to $N$ in configurations $\mathbf{R}_1$ to $\mathbf{R}_N$.

The term $B(\mathbf{R}_\mathrm{o}\dots\mathbf{R}_N)$ is the sum of all the interactions between particle 0 and others, in the same configurations.

The substitution of (32.12) into (32.11) leads to the expression (32.13):

$$\begin{aligned} \exp(-\mu/kT) = q/\left[\Lambda^3(N+1)\right] \cdot \int v..\int dR_\mathrm{o}\dots dR_N \exp(-\beta U_N) \\ \exp\left(-\beta B(\mathbf{R}_\mathrm{O}\dots\mathbf{R}_N)\right/\int v..\int d\mathbf{R}_1\dots d\mathbf{R}_N \exp(-\beta U_N) \end{aligned} \tag{32.13}$$

where

$$\exp(-\beta U_N)/\int v..\int d\mathbf{R}_1\ldots d\mathbf{R}_N\exp(-\beta U_N) = P(\mathbf{R}_1\ldots\mathbf{R}_N)$$

$P(\mathbf{R}_1\ldots\mathbf{R}_N)$ is the basic distribution function or density probability function to observe the configuration $\mathbf{R}_1\ldots\mathbf{R}_N$ (viz. Chap. 28).

The relation (32.12) can also be written:

$$\exp(-\mu/kT) = q/\left[\Lambda^3(N+1)\right]\cdot\int v\int d\mathbf{R}_o\ldots d\mathbf{R}_N P(\mathbf{R}_1\ldots\mathbf{R}_N)\exp[-\beta B(\mathbf{R}_O\ldots\mathbf{R}_N)] \tag{32.14}$$

At this point of the reasoning, we must remark that the term $\exp(-\beta B(\mathbf{R}_0\ldots\mathbf{R}_N)$ which quantifies the interactions between the added particle "0" and the other ones "1 to $N$" does not depend on the configuration $\mathbf{R}_1\ldots\mathbf{R}_N$ [the probability of which is $P(\mathbf{R}_1\ldots\mathbf{R}_N)$] but is on the dependence of the configuration $\mathbf{R}_O\ldots\mathbf{R}_N$. However, we can adopt a system of relative coordinates defined by the general expression:

$$\mathbf{R}_i' = \mathbf{R}_i - \mathbf{R}_0 \quad (\text{with } i \text{ from 1 to } N)$$

Then, the term $B(\mathbf{R}_O\ldots\mathbf{R}_N)$ becomes a function of the relative coordinates $\mathbf{R}_i'$, that is to say can be symbolized $B(\mathbf{R}_1'\ldots\mathbf{R}_N')$. Hence, one can write:

$$\exp(-\mu/kT) = q/\left[\Lambda^3(N+1)\right]\cdot\int d\mathbf{R}_o\int\ldots\int \mathrm{d}\mathbf{R}_1'\ldots d\mathbf{R}_N' P\left(\mathbf{R}_1'\ldots\mathbf{R}_N'\right)\exp\left[-\beta\left(\mathbf{R}_1'\ldots\mathbf{R}_N'\right)\right] \tag{32.15}$$

Then, after this transformation, one can take out $\mathbf{R}_0$ and integrate over. The integration gives $V$.

Given the fact that the integrand is the product of the exponential taking into account the sum $B$ (of all the interactions between the added particle and those constituting the initial system) and of the basic distribution $P(\mathbf{R}_N')$, it appears that the internal energy of the right-member of relation (32.14) is the average of the quantity $\exp[-\beta B(\mathbf{R}_1'\ldots\mathbf{R}_N')]$ in the ($T$, $V$, $N$) ensemble. Hence, we obtain:

$$\exp(-\mu/kT) = \left[q\,V/\Lambda^3(N+1)\right]\left\langle\exp\left((-B/kT\right)\right\rangle$$

After the replacement of $(N+1)/V$ by $N/V$ since $N+1\approx N$ and by introduction of:

$$\rho = N/V$$

we obtain:

$$\exp(-\mu/kT) = \left[q/\Lambda^3\rho\right]\langle\exp(-B/kT)\rangle$$

When all is done:

$$\mu = kT\ln\rho\Lambda^3/q - kT\ln\langle\exp(-B/kT)\rangle \tag{32.16}$$

or

$$\mu = kT\ln\Lambda^3/q + kT\ln\rho \ - kT\ln\langle\exp(-B/kT)\rangle \tag{32.17}$$

It is interesting to notice that the right member of (32.17) is the chemical potential of every gas, even if the studied fluid here, is a liquid. To be convinced, it is sufficient to consider its "mathematical structure." When the behavior of the fluid is actually ideal, there is no interaction and $B = 0$. Then the relation (32.17) becomes:

$$\mu \ = kT\ln\Lambda^3/q + kT\ln\rho$$

This expression is identical to that giving the chemical potential of a perfect gas.

$$\mu \ = \mu^{0\mathrm{g}} + kT\ln\rho \tag{32.18}$$

According to (32.17), the chemical potential of a real gas can be expressed by the relation:

$$\mu = \mu^{0\mathrm{g}} + kT\ln\rho \ - kT\ln\langle\exp(-B/kT)\rangle \tag{32.19}$$

## 32.5 A General Meaning of the Activity Coefficient

Hence, the last term of the right member (32.19) is the contribution to the value of the chemical potential of the interactions between molecules. $B$ is actually the interaction energy of the added particle with all others at the location $\mathbf{R}_1\ldots\mathbf{R}_N$ of the system.

When we compare the relation (32.18) with the relation (32.19) below:

$$\mu = \mu^{0\mathrm{g}} + kT\ln\rho + kT\ln\gamma \tag{32.20}$$

where $\gamma$ is the activity coefficient empirically introduced by Lewis in order to take into account the interactions between the particles, it appears that:

$$\gamma \equiv 1/\langle \exp(-B/kT)\rangle \tag{32.21}$$

Relation (32.19) is very important. It is the basis of the affirmation that activity coefficients take into account the particle interactions in the system. It provides a general expression of an activity $a$, in terms of statistical thermodynamics:

$$a = \rho/\langle \exp(-B/kT)\rangle$$

Moreover, by itself, relation (32.21) is a general expression of activity coefficients. However, these expressions cannot be considered as anything else than an approach to an activity because they are grounded in an approximation which is the "pairwise additivity" hypothesis.

## 32.6 The Chemical Potential and the Radial Distribution Function

Here, we mention one relation between the chemical potential and the radial distribution function. (Obtaining it is given in Appendix K). It is:

$$\mu = kT\ln\left(\rho \Lambda^3 q^{-1}\right) + \rho\int_0^1 d\xi \int_0^\infty U(R)g(R,\xi)4\pi R^2 dR \tag{32.22}$$

It has been set up by Kirkwood. From a general standpoint, it is based on the "pairwise additivity" hypothesis applied to the global potential energy. More precisely, it is founded on the virtual process consisting in coupling a particle with others bit by bit, all along the addition. It involves the presence of the coupling parameter $\xi$ which can vary from 0 up to 1. When $\xi = 0$, the added particle is not coupled to others, but the latter ones are coupled between themselves. When $\xi = 1$, it is fully coupled with others. For the intermediary values, $0 < \xi < 1$, the added particle is only partly coupled with others.

Hence, the term $\rho\int_0^1 d\xi \int_0^\infty U(R)g(R,\xi)4\pi R^2 dR$ is the work which has to be done in order the interactions of the particle with the others constituting the system to be effective. Let us symbolize the particle by $A$ and the work by $W(A|A)$. The left-hand $A$ figures the particle $A$ which is coupled. The right-hand one figures the kind of particles with which the previous one is coupled. In the occurrence, it is $A$ itself:

$$W\left(A\middle|A\right) = \rho\int_0^1 d\xi \int_0^\infty U(R)g(R,\xi)4\pi R^2 dR$$

Let us, already, notice that this relation is interesting because it directly leads to another expression of the activity coefficient of a gas. Actually,

$$kT\ln\left(\rho\Lambda^{3}q^{-1}\right) = kT\ln\left(\Lambda^{3}q^{-1}\right) + kT\ln\rho$$

By definition, the term $kT\ln(\Lambda^{3}q^{-1})$ is the standard potential in the gaseous phase:

$$kT\ln\left(\Lambda^{3}q^{-1}\right) = \mu^{\circ}\mathrm{g}$$

Relation (32.21) can also be written:

$$\mu = \mu^{\circ \mathrm{g}} + kT\ln\rho - \rho\int_{0}^{1} d\xi \int_{0}^{\infty} U(R\ )g(R,\xi)4\pi R^{2}dR$$

By comparison with the classical expression:

$$\mu = \mu^{\circ \mathrm{g}} + kT\ln\rho + kT\ln\gamma^{\mathrm{g}}$$

where $\gamma^{\mathrm{g}}$ is the activity coefficient of the gas.

Hence, the term $\rho\int_{0}^{1} d\xi\int_{0}^{\infty} U(R)g\ (R,\xi)4\pi R^{2}dR$ is an expression of the activity coefficient.

Relation (32.22) proves to be very interesting for a study of activity coefficients.

## 32.7 Relation Between the Chemical Potential and the Function *G*

We have already introduced the function $G$ (cf. Chap. 31). It involves the radial distribution function. It is given by the relation:

$$G = \int_{0}^{\infty} \left[g\left(\overline{R}\right) - 1\right]4\pi R^{2}dR$$

It results from the theory of grand ensemble.

It is also possible to express the chemical potential $\mu$ starting from $G$ with the help of the relation which we establish below. It involves the isothermal compressibility coefficient of the system. The expression which links both quantities is:

$$\mu(\rho) = \int kT\left[d\rho/\left(\rho + \rho^{2}G\right)\right] + \text{constant} \qquad (32.23)$$

Therefore, once the change in $G$ as a function of the density number $\rho$ is known, one can conceive that the chemical potential can be obtained, the fact that $G$ is accessible through $g(R)$ being well understood. Evidently, the relation (32.23) is one integral solution of the expression (32.24):

$$(\partial\mu/\partial\rho)_T = kT/\left(\rho+\rho^2G\right) \tag{32.24}$$

The way followed to obtain the latter is postponed to the end of this paragraph. Relation (32.23) can also be equivalently written according to (32.25). Hence, the integration can be done from it:

$$\mu(\rho) = kT\int dr\,[1/\rho - G/(1+\rho G)] \quad + \text{ constant} \tag{32.25}$$

During the integration, the following mathematical difficulty happens: when $\rho = 0$, the chemical potential does not exhibit a finite value. The trick used to overcome it is as follows. Let us consider a solution of very low density $\rho_0$ ($\rho_0 \to 0$). In these conditions, the interactions between molecules are negligible. Then, the chemical potential $\mu(\rho_0)$ is expressed according to a relation which is of the same type as that which is encountered with the perfect gases:

$$\mu(\rho_0) = kT\ln\left(\rho_0\Lambda^3q^{-1}\right)$$
$$\mu(\rho_0) = kT\ln\left(\Lambda^3q^{-1}\right) + kT\ln\rho_0$$

The first term of the right member is nothing else than the chemical standard potential $\mu^{\circ g}$ of the liquid when it is in the gaseous state, as its mathematical structure shows it. As a result,

$$\mu(\rho_0) = \mu^{\circ g} + kT\ln\rho_0$$

Hence, one can integrate from the lower limit $\rho_0$ (and not from 0) up the limit ρ, given the expression:

$$kT\int_0^\rho d\rho'[1/\rho' - G/(1+\rho'G)] = \mu^{\circ g} + kT\ln\rho_0 + \ kT\int \rho_0^\rho[1/\rho' - G/(1+\ \rho'G)]d\rho'$$

whence:

$$\mu(\rho) = \mu^{\circ g} + kT\ln\rho - kT\int_0^\rho [G/(1+\rho'G)]d\rho' \tag{32.26}$$

A relation between the function *G* and the activity coefficient must now be found.

Evidently, it can be done through the integration of the latter expression. According to what is preceding, we know that:

$$kT \ln\langle \exp(-B/kT)\rangle \ = \ kT\int_o^{\rho} [G/(1+\rho' G)]d\rho'$$

Hence, we can deduce that the work of coupling of a molecule with all the others is equal to the necessary work to increase the system density from 0 up to the final one $\rho$. Hence, the relation (32.26) permits to find another expression of the activity coefficients, which is:

$$\ln\gamma = -\int_o^{\rho} [G/(1+\rho' G)]d\rho' \tag{32.27}$$

As a result, thanks to this expression, it is possible to link the activity coefficient to the radial distribution function $g(R)$ through the function $G$.

The relation (32.26) will be generalized to systems consisting in fluid mixtures. This possibility is demonstrated by the Kirkwood–Buff's theory (viz. Chaps. 42 and 44).

- *Obtention de la relation (32.24)*

*The demonstration is given in Chap. 31. Let us only recall that it involves the isothermal compressibility coefficient $k_T$ and that it involves the following equalities already demonstrated:*

$$(\partial\rho/\partial\mu)_T = (\partial\rho/\partial p)_T(\partial p/\partial\mu)_T$$

$$(\partial\rho/\partial p)_T \ = \ \rho\kappa_T$$

$$(\partial p/\partial\mu)_T \ = \ \rho$$

$$(\partial\mu/\partial p)_T \ = 1/\,\rho^2\kappa_T$$

$$kT\rho\kappa_T \ = \ 1+\rho G$$