1

Pure Liquids

This chapter will be given over to atomic and molecular liquids. A pure molecular liquid is a liquid comprising only one type of non-dissociated molecules. The study of liquids is more difficult than that of gases and solids because they are in an intermediary state, structurally speaking. Indeed, as is the case with solids, we can imagine that in liquids (and this is confirmed by X-ray diffraction), the interactions between molecules are sufficiently powerful to impose a sort of order within a short distance of the molecules. However, the forces involved in these interactions are sufficiently weak for the molecules to have relative mobility and therefore for there to be disorder (no form of order) when they are far apart, as is the case with gases.

1.1. Macroscopic modeling of liquids

In the areas where liquids are typically used, far from the critical conditions, it is often possible to consider liquids to be incompressible – meaning that $\left(\partial V/\partial P\right)_T \cong 0$ – but dilatable. The order of magnitude of a dilation coefficient is 10^{-3} degrees^{-1}, whereas that of the compressibility coefficient is 10^{-4}atm^{-1}.

As we approach the critical conditions, this approximation is no longer possible, and the properties of the liquid tend more to be governed by an equation of state. Whilst the "cubic" equations of state for gases do include critical conditions, it is accepted that the properties of liquids often necessitate equations of state that take account of the intervention of forces when more than two bodies are concerned. Additionally, the third- and fourth coefficients of the virial, which can no longer be ignored in the case of liquids, become necessary when these types of forces are at work.

Certain equations of state specific to liquids have been put forward in the literature, including Rocard's, which is written thus:

$$P = \frac{\mathrm{R}TV^2}{(V - b/3)^3} - \frac{a}{V^2} \qquad [1.1]$$

In addition, this equation, expressed as the expansion of the virial, assumes the form:

$$PV = RT\left\{\begin{array}{l} 1 + \left(b - \dfrac{a}{RT}\right)\dfrac{1}{V} + \left(\dfrac{ab}{RT} - \dfrac{b^2}{3}\right)\dfrac{1}{V^2} \\ + \left(\dfrac{b^3}{27} - \dfrac{ab^2}{3RT}\right)\dfrac{1}{V^3} + \dfrac{ab^3}{3RT}\dfrac{1}{V^4} \end{array}\right\} \qquad [1.2]$$

This equation does indeed include the third and fourth coefficients of the virial.

The heat capacities at constant volume and constant pressure are practically identical, around 0.5cal/g, or 2.1kJ/kg.

1.2. Distribution of molecules in a liquid

On a structural level, liquids are classified into two categories: *associated liquids* and *non-associated liquids*.

A liquid is said to be *non-associated* if the intra-molecular degrees of freedom (rotational, vibrational, electronic and nuclear) are not majorly disturbed by the proximity of neighboring molecules. These liquids can be treated, as is the case with gases, with independence between the internal motions and the translation of the molecules.

A liquid is said to be *associated* if, unlike in the previous case, the molecule's internal degrees of freedom are disturbed by the proximity of other molecules. This disturbance may be so great that, in practical terms, we need to consider associations between molecules, coming together to form dimers, trimers, etc. The new bonds that need to be taken into account are usually hydrogen bonds, whose energy is 4-5 times less than that involved in typical chemical bonds, but which are 4-5 times stronger than intermolecular bonding by van der Waals forces. When the temperature rises, these bonds are broken and, particularly when the thermal agitation energy ($k_B T$) is much greater than the energy in the hydrogen bond, the molecules separate and regain individuality when they are near to the gaseous state.

These associations lend associated liquids very special properties, such as anomalies of the dilation coefficient, high viscosity, low surface tension and a high boiling point. Liquid water belongs to this category. The best way of dealing with these liquids in thermodynamics is to consider them no longer as pure liquids, but rather to treat them as associated solutions, with dimeric, trimeric (etc.) molecules – see section 2.5.

1.2.1. *Molecular structure of a non-associated liquid*

Hereinafter, we shall focus only on non-associated liquids, and we shall suppose the molecules are spherical. A non-associated liquid is characterized by a local order, or short-distance order. The best illustration of this is of liquid metals. In Figure 1.1, which gives a 2-dimensional image of the arrangement of spherical molecules in a liquid, we can see that the molecules are relatively close together, and that around each molecule, there is an area of order which is illustrated by the circles superimposed on the figure. The short-distance arrangement, within the circles, is almost identical to the molecular arrangement in a solid crystal but, unlike with a crystal, there is no long-distance order. The two circles on Figure 1.1 exhibit no periodicity.

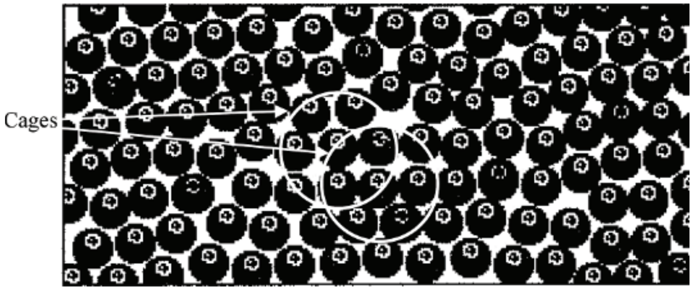

Figure 1.1. *Two-dimensional diagram of the distribution of molecules in a liquid*

The second difference between a crystal and a liquid is that in the latter, the molecules are in perpetual motion, so Figure 1.1 is representative of the situation only at a given time. Unlike with a solid crystal, the distribution of those molecules would be different an instant later, although we would find similar zones of ordered arrangement.

Hence, in order to accurately describe a liquid, we cannot content ourselves with merely describing the position of a few appropriately-chosen neighboring molecules, as we can with the lattice of the crystal. We would have to define the positions of each of the molecules at every moment in time. In view of the impossibility of the task in a medium with normal dimensions (around a mole, which contains 10^{23} molecules), we use statistical methods using so-called *correlation functions*. The paired correlation function which we intend to examine constitutes the first level of this description.

1.2.2. *The radial distribution function*

Throughout this chapter, we shall suppose that the interactions between N particles of a liquid medium are additive and paired, meaning that the internal energy due to these interactions is merely the sum of the interactions between molecules, two by two. Thus, the internal energy is the sum of the energies between the molecules taken two by two $\varepsilon_{i,j}\left(r_{i,j}\right)$. This energy depends only on the distance between the two molecules. Hence, we have:

$$U(1,2,...N)=\sum_{i<j}^{N}\varepsilon_{i,j}\left(r_{i,j}\right) \qquad [1.3]$$

Consider a molecule chosen at random in the structure (Figure 1.2). Let d$N(r)$ signify the number of molecules whose centers are situated in the crown between the two spheres centered on the chosen molecule, with radii r and r+dr and volume $4\pi\, r^2$dr. The density of molecules in the crown $\rho(r)$, i.e. the number of molecules situated in the crown per unit volume of that spherical crown, at a distance r from the central molecule, is such that:

$$\rho(r)=\left(\frac{\mathrm{d}N(r)}{\mathrm{d}V(r)}\right)_r=\frac{1}{4\pi r^2}\frac{\mathrm{d}N(r)}{\mathrm{d}r} \qquad [1.4]$$

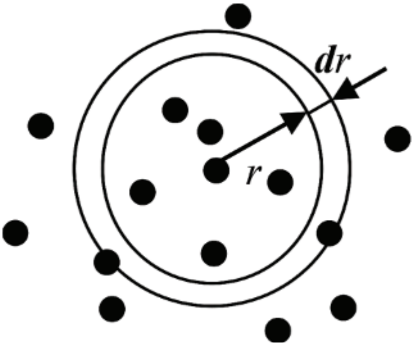

Figure 1.2. *Arrangement of molecules of liquid around the center of a cage*

The volumetric density ρ is defined as the ratio of the total number of molecules in the liquid in question to the volume of that liquid, i.e.:

$$\rho = \frac{N}{V} \quad [1.5]$$

We define the paired correlation factor or the radial distribution function *g(r)* by the relation:

$$g(r) = \frac{\langle \rho(r) \rangle}{\rho} \quad [1.6]$$

As we can see, this function is the ratio of the mean value of the local density of molecules (mean calculated at the positions, at a given time and over a period of time) to the volumetric density of molecules. The correlation factor *g(r)* is proportional to the probability of finding a molecule at a distance $r + \mathrm{d}r$ from another molecule. Thus, we can write the relation:

$$g(r) = \frac{1}{\rho N} \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \delta_{i,j} \left[r - r_{i,j} \right] \right\rangle \quad [1.7]$$

where $\delta_{i,j}$ is the Kronecker delta, such that: $\begin{cases} \delta_{i,j} = 0 \text{ if } i \neq j \\ \delta_{i,j} = 1 \text{ if } i = j \end{cases}$

This ratio [1.7] quantifies the local structure – in other words, the way in which the molecules are arranged in relation to one another.

1.2.3 *The curve representative of the radial distribution function*

By combining relations [1.4] and [1.6], we see that the mean number of molecules in the coronal volume between the spheres with radii r and $r + \mathrm{d}r$ will be:

$$\left\langle \mathrm{d}N(r) \right\rangle = 4\pi \rho r^2 g(r)\,\mathrm{d}r \qquad [1.8]$$

In the solid crystal, only certain distances exist, and the representative curve for the function $g(r)$ exhibits extremely slender peaks for these distances.

In the case of the liquid, the curve representing the function $g(r)$ has the shape shown in Figure 1.3. We obtain a first peak with a breadth $\Delta r/r$ of several %, which represents the distance between the first neighbors. The next peaks, which represent the second, third (etc.) neighbors, are heavily damped because of the disorder over a long distance. The function $g(r)$ tends toward 1 at a long distance, there is no longer order and therefore, on average, we always find the same number of molecules per unit volume as are present in the overall liquid.

Figure 1.3 can be obtained by neutron diffraction or hard, very penetrating X-ray diffraction, such as those produced by synchrotron sources.

In principle, the distribution $g(r)$ is null for distances less than 0.5 Ä, because there is no chance of finding two molecules that close together, given that the order of magnitude of a molecule's diameter is between 1 and 3 Ä. Around values between 3 and 5 Ä, molecules may be found, and the local density is greater than the overall density. Thus, $g(r)$ is greater than 1. Between the first series of neighbors and the second, there are few molecules, and the factor $g(r)$ drops back below 1. The second maximum corresponds to the second neighbors, which are less precisely localized, and therefore have lower local densities – hence the damping effect seen here.

The more the peaks are damped, the more negligible the influence of the central atom. Thus, it is easy to understand that we can often content ourselves with the influence of the nearest neighbors, i.e. those which correspond to the first peak.

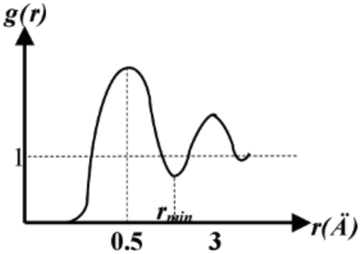

Figure 1.3. *Paired distribution function for a liquid*

We can see that, apart for a few exceptions, the local order and the intermolecular distances of the maxima are the same in the solid and the corresponding liquid. The peaks shown in the solid are very slender, but the first peak is situated at the same value of *r*.

Diagrams such as Figure 1.3 are very useful, because they enable us to calculate two statistical values:

– the mean distance of the first neighbors. This value is given by the first maximum point on the curve. The breadth of the peaks shows the variation of the distances around the mean value due to the ordering of the molecules and to their agitation;

– the mean value of the number of first neighbors. To calculate this, we decide that the first neighbors are those which are found at distances between 0 and r_{min}. This value is the abscissa of the minimum which follows the first maximum (see Figure 1.3) on the plot of $g(r)$. Thus, for the number of first neighbors, we can write:

$$z = \int_0^{r_{\min}} \mathrm{d}N(r) = 4\pi\rho \int_0^{r_{\min}} r^2 g(r)\,\mathrm{d}r \qquad [1.9]$$

In a liquid, unlike with a crystal, this number may not necessarily be an integer.

1.2.4. *Calculation of the macroscopic thermodynamic values*

We shall show that, like the partition function, the radial distribution function contains all the information pertaining to the thermodynamic definition of the liquid. Therefore, it can be used to calculate the macroscopic values such as the internal energy, the pressure, an equation of state or the heat capacities.

On the basis of relation [1.8], we can write the differential of the internal energy due to the interactions in the form:

$$\mathrm{d}u = \frac{4\pi r^2 \rho g(r)\varepsilon(r)\,\mathrm{d}r}{2} \qquad [1.10]$$

Hence, by integrating over the whole volume:

$$\frac{U - U_{pf}}{\mathrm{R}T} = \frac{\rho}{2\mathrm{k_B}T}\int_0^\infty 4\pi r^2 g(r)\varepsilon(r)\,\mathrm{d}r \qquad [1.11]$$

U_{pf} denotes the internal energy of a fluid with no interaction, i.e. the molar internal energy of the perfect gas which, according to the theorem of equal distribution of energy, has the value:

$$U_{pf} = \frac{3\mathrm{R}T}{2} \qquad [1.12]$$

From this, we can deduce the internal energy:

$$\frac{U}{\mathrm{R}T} = \frac{3}{2} + \frac{\rho}{2\mathrm{k_B}T}\int_0^\infty 4\pi r^2 g(r)\varepsilon(r)\,\mathrm{d}r \qquad [1.13]$$

As we have the expression of the internal energy, which is a characteristic function in variables *V* and *S*, we have all the necessary information to define the phase.

To calculate the pressure, we need to have the differential of the internal energy in variables *P* and *T*, an expression which is of the form:

$$\mathrm{d}U = T\left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T - \left[P + \left(\frac{\partial P}{\partial T}\right)_V\right]\mathrm{d}V \qquad [1.14]$$

Then, we calculate the pressure on the basis of the derivative of the internal energy in relation to the volume, which gives us:

$$\frac{P}{\rho \mathrm{R}T} = 1 - \frac{2\pi \mathrm{N}_{\mathrm{a}}^{2}\rho}{3\mathrm{k}_{\mathrm{B}}T}\int_{0}^{\infty} r^{2} g(r)\left[\frac{\mathrm{d}\varepsilon(r)}{\mathrm{d}r}\right]\mathrm{d}r \qquad [1.15]$$

By substituting the value of *r* found in relation [1.5], written for one mole, back into the above expression, then it is easy to write the equation of state:

$$PV = n\mathrm{N}_{\mathrm{a}}\left\{1 - \frac{2\pi \mathrm{N}_{\mathrm{a}}^{2}\rho}{3\mathrm{k}_{\mathrm{B}}T}\int_{0}^{\infty} r^{2} g(r)\left[\frac{\mathrm{d}\varepsilon(r)}{\mathrm{d}r}\right]\mathrm{d}r\right\}RT \qquad [1.16]$$

Similarly, the material derivative of the internal energy in relation to the temperature enables us to easily calculate the heat capacity at constant volume.

We can now calculate all the other functions, particularly the compressibility at constant temperature χ_T, which gives us:

$$\chi_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1 + \mathrm{N}_{\mathrm{a}}\int_V [g(r) - 1] 4\pi r^2 dr}{\mathrm{R}T} \qquad [1.17]$$

Thus, we have shown that knowing the radial distribution function enables us to completely define the phase in thermodynamic terms.

We know that a second way of calculating the macroscopic values is to use the canonical partition function. This is the method that we shall use from hereon in. To do so, we must construct a structure of the liquid, in order to be able evaluate the terms of interaction in the canonical partition function. Various techniques are used. We shall describe four such techniques: Guggenheim’s and Mie’s models, extrapolated respectively from the gas and solid models, the Lennard-John and Devonshire cellular model and the cell/vacancy model.

1.3. Models extrapolated from gases or solids

In light of the proximity of the structure of liquid, firstly to that of a gas (in terms of the mobility of the molecules and the disorder at long distance) and secondly to that of a solid (in terms of the presence of an order over a short distance and figures of X-ray diffraction), the earliest models developed were extrapolations either from a model of a gas or from one of a solid. These models can be used to calculate the radial distribution function and the canonical partition function. As we know that only one of the two is necessary, in our discussion below, we shall restrict ourselves to calculating the canonical partition function.

1.3.1. *Guggenheim's smoothed potential model*

This model [GUG 32] is extrapolated from the imperfect gas model, which can be used to calculate the second coefficient of the virial (see section A.3.4 in Appendix 3). The canonical partition function then takes the form of equation [A.3.41].

From this, we deduce the configuration integral due to the interactions and to the volume, in this case the volume of slightly imperfect gases:

$$I_I = \frac{V^N}{N!}\left(1 - \frac{N^2 B_{\mathrm{AA}}(T)}{V}\right)^N \qquad [1.18]$$

Using the notation v_m to represent the volume per molecule (V/N), or the molecular volume (which must not be confused with the volume of a molecule), and using Stirling's approximation [A.3.1], this expression takes the following equivalent form:

$$I_I = \exp(N)\left(v_m - B_{\mathrm{AA}}(T)\right)^N \qquad [1.19]$$

According to relation [A.3.40], the term B_{AA} is a function only of the temperature.

We can use such an expression for a highly-imperfect gas or a liquid, supposing that the term B_{AA} is also a function of the volume. The difference v_m-$B_{\mathrm{AA}}(T,v_m)$ will therefore represent the free volume per molecule v_f and the above relation will then be written:

$$I_I = \exp(N)\left(v_f(v_m)\right)^N \qquad [1.20]$$

Supposing the potential function to be more or less constant, an initial model of the liquid state was proposed.

Thus, we suppose that each molecule moves through a uniform field of potential, the lattice energy, $(-\varepsilon)$ (attractive) which will be determined by the mean number of near neighbors at a given distance from the molecule, and will essentially be a function of the number of molecules per unit volume, i.e. a function of the volume per molecule v_m. The contribution of the interactions to the canonical function can thus be written by supplementing it with the exponential term corresponding to that uniform potential. Thus, we obtain:

$$I_I = \exp(N)\left(v_f(v_m)\right)^N \left[\exp\left(\frac{\varepsilon(v_m)}{\mathrm{k_B}T}\right)\right]^N \qquad [1.21]$$

This can also be written as:

$$I_I = \left[\exp(1) v_f(v_m) \exp\frac{\varepsilon(v_m)}{\mathrm{k_B}T}\right]^N \qquad [1.22]$$

Hence, in light of relation [A.3.42], and with Stirling's approximation applied, the canonical partition function for the fluid will be written thus:

$$\ln Z_C = \frac{N\varepsilon(v_m)}{\mathrm{k_B}T} + N\ln\left(\frac{\left(2\pi m \mathrm{k_B}T\right)^{3/2} v_f(v_m)}{\mathrm{h}^3}\right) \\ +N + N\ln z_{\mathrm{int}} - N\ln N \qquad [1.23]$$

On the basis of relations [1.23] and [A.3.48], we can calculate the Helmholtz energy F:

$$\frac{F}{N} = -\varepsilon(v_m) - \mathrm{k_B}T\ln\left(\frac{\left(2\pi m \mathrm{k_B}T\right)^{3/2} v_f(v_m)}{\mathrm{h}^3}\right) \\ -\mathrm{k_B}T - \mathrm{k_B}T\ln z_{\mathrm{int}} \qquad [1.24]$$

From this, we deduce the pressure:

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{\partial \varepsilon(v_m)}{\partial v_m} + \mathrm{k_B}T\frac{\partial \ln v_f(v_m)}{\partial v_m} \qquad [1.25]$$

Most of the time, the properties of the liquid are insensitive to variations in pressure and it is therefore correct to consider the pressure to be zero. Thus, we shall have:

$$\frac{\partial \varepsilon(v_m)}{\partial v_m} + \mathrm{k_B}T\frac{\partial \ln v_f(v_m)}{\partial v_m} \cong 0 \qquad [1.26]$$

Hence, the compressibility factor $Z = PV/\mathrm{R}T$ is essentially null regardless of the volume.

The molecular Gibbs energy is:

$$\begin{aligned}\frac{G}{N} &= \frac{F}{N} + P\frac{V}{N}\\ &= -\varepsilon - \mathrm{k_B}T\ln\frac{\left(2\pi m\mathrm{k_B}T\right)^{3/2} v_f}{\mathrm{h}^3} - \mathrm{k_B}T - \mathrm{k_B}T\ln z_{\mathrm{int}} + Pv_m\end{aligned} \qquad [1.27]$$

The molecular internal energy is given by:

$$\frac{U}{N} = -T^2\left(\frac{\partial(F/T)}{\partial T}\right) = -\varepsilon + \frac{3}{2}\mathrm{k_B}T + \frac{U_{\mathrm{int}}}{N} \qquad [1.28]$$

Thus, the molecular enthalpy is:

$$\frac{H}{N} = \frac{U}{N} + P\frac{V}{N} = -\varepsilon + \frac{3}{2}\mathrm{k_B}T + \frac{U_{\mathrm{int}}}{N} + Pv_m \qquad [1.29]$$

The molecular entropy is given by:

$$\begin{aligned}\frac{S}{N} &= -\frac{\partial \frac{F}{N}}{\partial T} = \mathrm{k_B}\ln\left(\frac{\left(2\pi m\mathrm{k_B}T\right)^{3/2} v_f v_m)}{\mathrm{h}^3}\right)\\ &\quad + \frac{5}{2}\mathrm{k_B} + \mathrm{k_B}T\frac{\partial \ln v_f}{\partial T} + \mathrm{k_B}\ln z_{\mathrm{int}}\end{aligned} \qquad [1.30]$$

In view of the variation of the free volume with temperature (see section 1.3.3) and of the independence of the volume from pressure ($\chi_T \approx 0$), we find:

$$\frac{S}{N} = \mathrm{k_B} \ln\left(\frac{\left(2\pi m \mathrm{k_B} T\right)^{3/2} v_f)}{\mathrm{h}^3}\right) - \mathrm{k_B} \ln\frac{1}{v_m} + \frac{5}{2}\mathrm{k_B} + \mathrm{k_B} \ln z_{\mathrm{int}} \qquad [1.31]$$

In relations [1.27], [1.28] and [1.29], the pressure can be taken to be null, in keeping with relation [1.26].

1.3.2. *Mie's harmonic oscillator model*

This time referring to the local order in a liquid similar to that of a solid, the potential function is given a form very similar to that of a harmonic oscillator. Thus, a second model of the liquid state [MIE 03] was put forward. Beginning with the quasi-crystalline model of a liquid, we suppose that each molecule is in a field of potential whose minimum is $\varepsilon_0(v_m)$, and that the molecule moves through that field corresponding to a three-dimensional harmonic oscillator of frequency ν, which is also a function of the volume per molecule v_m. We use the symbol r to denote the distance from the center of the molecule to the center of the cavity where the minimum potential is in force. At that distance, the molecule would have a potential energy $-(\varepsilon_0 + \mathrm{k_B}T) + \frac{m(2\pi\nu)^2 r^2}{2}$ so, if we integrate for all possible positions of the molecule, the configuration integral for the partition function is found to be:

$$I_I = \exp\left[N\frac{(\varepsilon_0 + \mathrm{k_B}T)}{\mathrm{k_B}T}\right]\left[\int_0^\infty 4\pi r^2 \exp\left(-\frac{m(2\pi\nu)^2 r^2}{2\mathrm{k_B}T}\right)\mathrm{d}r\right]^N \qquad [1.32]$$

After integration, this gives us:

$$I_I = \left\{\exp\left[\frac{(\varepsilon_0 + \mathrm{k_B}T)}{\mathrm{k_B}T}\right]\left(\frac{\mathrm{k_B}T}{2\pi m\nu^2}\right)^{3/2}\right\}^N \qquad [1.33]$$

Using approximation [A.3.31] for the vibration, the complete canonical partition function is then written:

$$Z_C = \left[z_{\text{int}} \left(\frac{2\pi m \mathrm{k_B} T}{\mathrm{h}^2} \right)^{3/2} \left(\frac{\mathrm{k_B} T}{\mathrm{h}\nu} \right)^3 \right]^N I_1 \quad [1.34]$$

Hence, if we take relation [1.33] into account:

$$Z_C = \left[z_{\text{int}} \left(\frac{2\pi m \mathrm{k_B} T}{\mathrm{h}^2} \right)^{3/2} \right]^N \left\{ \exp\left[\frac{(\varepsilon_0 + \mathrm{k_B} T)}{\mathrm{k_B} T} \right] \left(\frac{\mathrm{k_B} T}{2\pi m \nu^2} \right)^{3/2} \right\}^N \quad [1.35]$$

By switching to logarithms, we obtain:

$$\ln Z_C = \frac{N\varepsilon_0(v_m)}{\mathrm{k_B} T} + 3N \ln\left(\frac{\mathrm{k_B} T}{\mathrm{h}\nu(v_{\mathrm{m}})} \right) + N + N \ln z_{\text{int}} \quad [1.36]$$

This is the partition function of the liquid, given by Mie’s 3D harmonic oscillator model.

Based on relations [1.36] and [A.3.48], we find that the Helmholtz energy per molecule is:

$$\frac{F}{N} = -\varepsilon_0 - 3\mathrm{k_B} T \ln\left(\frac{\mathrm{k_B} T}{\mathrm{h}\nu} \right) - \mathrm{k_B} T - \mathrm{k_B} T \ln z_{\text{int}} \quad [1.37]$$

In the same way as we did above, we deduce the expressions for the different functions:

$$P = -\frac{\partial F}{\partial V} = \frac{\partial \varepsilon_0}{\partial v} - 3\mathrm{k_B} T \frac{\partial \ln v_f}{\partial v_m} \cong 0 \quad [1.38]$$

$$\frac{G}{N} = -\varepsilon_{0N} - 3\mathrm{k_B} T \ln \frac{\mathrm{k_B} T}{\mathrm{h}\nu} - \mathrm{k_B} T - \mathrm{k_B} T \ln z_{\text{int}} + P v_m \quad [1.39]$$

$$\frac{U}{N} = -\varepsilon_0 + 3\mathrm{k_B} T + \frac{U_{\text{int}}}{N} \quad [1.40]$$

$$\frac{H}{N} = -\varepsilon_0 + 3\mathrm{k_B}T + \frac{U_{\mathrm{int}}}{N} + Pv_m \qquad [1.41]$$

In all these relations, the term Pv_m is negligible.

The entropy per molecule is given by:

$$\frac{S}{N} = -\frac{\partial\left(\frac{F}{N}\right)}{\partial T} = 3\mathrm{k_B}\ln\left(\frac{\mathrm{k_B}T}{\mathrm{h}\nu}\right) + 4\mathrm{k_B} + \mathrm{k_B}\ln z_{\mathrm{int}} \qquad [1.42]$$

This expression is independent of the volume.

Thus, we obtain two different series of expressions. We usually use the smoothed potential model we link the properties of gases to those of liquids, and the harmonic oscillator model to link the properties of liquids to those of solids.

NOTE 1.1.– Relations [1.24] and [1.37] may be identical for a certain temperature and a certain volume per molecule, identifying ε with ε_0 and attributing the following value for the molecular volume:

$$v_m = \left(\frac{\mathrm{k_B}T}{2\pi m\nu^2}\right)^{3/2} \qquad [1.43]$$

1.3.3. *Determination of the free volume on the basis of the dilation and the compressibility*

The free volume of the liquid, which we need to know in order to exploit Guggenheim’s model, can be determined by a variety of methods: velocity of propagation of sound, vapor pressure, measurements of dilatation and compressibility. We have chosen to discuss this latter method.

In view of their definitions, the volumetric dilation coefficient and compressibility coefficient enable us to write:

$$\frac{\beta}{\chi_T} = -\frac{(\partial V/\partial T)_{P,N}}{(\partial V/\partial P)_{T,N}} = \left(\frac{\partial P}{\partial T}\right)_{V,N} \qquad [1.44]$$

In light of relation [1.26] (with ε and v_f being functions only of v_m), we can write:

$$\left(\frac{\partial P}{\partial T}\right)_{V,N} = \mathrm{k_B}\frac{\partial \ln v_f}{\partial v_m} \qquad [1.45]$$

However, if we consider that the molecules are arranged in a cubic lattice with centered faces, spaced the length a apart, we can take the following value for the free volume for the molecules:

$$v_f = \frac{4\pi}{3}(a-D)^3 \qquad [1.46]$$

Using relation [1.51], which we shall demonstrate later on (see relations [1.50] and [1.51] in section 1.4), we can write:

$$\frac{\partial \ln v_f}{\partial v_m} = \frac{\left(\frac{4\pi}{3}\sqrt{2}\right)^{1/3}}{v_m^{2/3} v_f^{1/2}} \qquad [1.47]$$

By substituting this value back into equations [1.44] and [1.45], we find the value of the molecular free volume:

$$v_f = \frac{4\pi\sqrt{2}\mathrm{k_B}^{1/3}\chi_T^3}{3v_m^2\beta^3} \qquad [1.48]$$

If, for β and χ_T, we take orders of magnitude of, respectively, $10^{-3}\mathrm{K}^{-1}$ and $10^{-4}\mathrm{atm}^{-1}$, we obtain, e.g. for chloroform:

$$\mathrm{N_a} v_f = 0.44\ \mathrm{cm^3/mole} \qquad [1.49]$$

This value is perfectly acceptable.

1.4. Lennard-Jones and Devonshire cellular model

This model [LEN 37] is based on Figure 1.4. Each molecule is inside a spherical cage – the cell – whose radius is a. This sphere is the molecule's mean sphere of influence.

The energy of interaction between two molecules is expressed by Lennard-Jones' relation [A.3.44]. This interaction is limited to the molecule's z nearest neighbors.

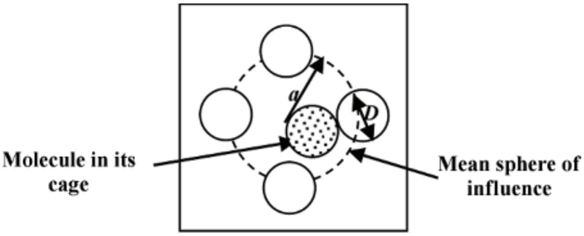

Figure 1.4. *Cage and molecules of liquid*

This number z is the coordination index linked to the cell geometry. We shall suppose that the molecules occupy the sites of a cubic lattice with centered faces, and therefore the coordination index is $z = 12$.

The volume of liquid is divided into cells centered on each molecule, whose near neighbors occupy the medium from the vertices of a cube with side length $2a/\sqrt{2}$. Each molecule which is a near neighbor of the original one thus belongs to four cells, and each cell contains 1 + 12/4 = 4 molecules. Hence, the volume of the cell is such that:

$$4v_m = 8a^3 / \left(\sqrt{2}\right)^3 \qquad [1.50]$$

and therefore:

$$a^3 = v_m \sqrt{2} \qquad [1.51]$$

The translational canonical partition function with interactions can be written, on the basis of expression [A.3.38], taking account only of the z molecules that are near neighbors of each molecule i.

$$Z_{C(t)} = \frac{1}{N!}\left(\frac{z_{pf}}{V}\right)^N \int\int_V \ldots \int \exp - \frac{\sum_{i=1}^{N}\sum_{j=1}^{z} \varepsilon_{i,j}\left(\omega^N\right)}{\mathrm{k_B}T} (\mathrm{d}\,\omega)^N \qquad [1.52]$$

On the basis of relation [A.3.24], using $\varepsilon\left(\omega^N\right)$ to denote the double sum appearing in the previous relation, the canonical partition function becomes:

$$Z_{C(t)} = \frac{1}{N!}\left[\frac{\mathrm{h}}{\left(2\pi m \mathrm{k_B} T\right)^{1/2}}\right]^{-3N} \iiint\limits_{V} \cdots \int\limits_{V} \exp\left(-\frac{\varepsilon\left(\omega^N\right)}{\mathrm{k_B}T}\right)(\mathrm{d}\omega)^N \qquad [1.53]$$

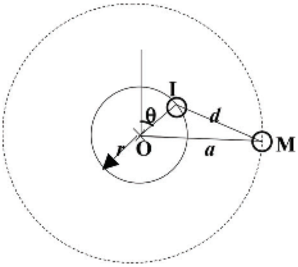

Figure 1.5. *Distance between a molecule and one of its near neighbors*

We shall now evaluate the double sum $\varepsilon\left(\omega^N\right)$. The near neighbors of a molecule i are, in fact, situated at different distances d_{ij} from it, and those distances change over time. Rather than moving both the molecule i and its near neighbors at once, we shall suppose that the center of the cell is stationary, that the molecule i moves in concentric circles of radius r around that center, and that the near neighbors are affixed to a concentric sphere with radius a. The radius r varies between 0 and a. Consider the plane passing through the molecule i at point I, one of its near neighbors at M and the center of the cell O (Figure 1.5).

In order to simplify the multiple integration appearing in expression [1.53], we shall create spherical symmetry and average the distance from the atom i along a radius r to all its near neighbors. The energy $\varepsilon\left(\omega^N\right)$ can be written:

$$\varepsilon\left(\omega^N\right) = \frac{Nz}{2}\varepsilon(a) + \frac{z}{2}\sum_{i=1}^{N}\left[\left\langle \varepsilon(d)\right\rangle - \varepsilon\left(a\right)\right] \qquad [1.54]$$

$\langle \varepsilon(d) \rangle$ is the mean mutual energy between the atom *i* and a near neighbor when the atom *i* is on the disc of radius *r*. This energy is a function of the distance, which is given by the following equation (see Figure 1.5):

$$d = \sqrt{r^2 + a^2 + 2ar\cos\theta} \qquad [1.55]$$

The mean energy is:

$$\langle \varepsilon(d) \rangle = \int_0^{\pi} \varepsilon(d) \sin\theta \, \mathrm{d}\theta \qquad [1.56]$$

Using relation [A.3.44] for the potential energy of interaction and substituting into it the value given by relation [1.55], we find:

$$\langle \varepsilon(d) \rangle = \frac{Nz\varepsilon_0}{2}\left[\left(\frac{d_0}{a}\right)^{12} \mathrm{l}\left(\frac{d^2}{a^2}\right) - 2\left(\frac{d_0}{a}\right)^{6} \mathrm{m}\left(\frac{d^2}{a^2}\right)\right] \qquad [1.57]$$

with the following meaning for the functions “l” and “m” that appear in equation [1.57]:

$$\mathrm{l} = \frac{a^2}{d^2}\left\{\left(\begin{array}{c} 1 + 12\dfrac{d^2}{a^2} + 50\left(\dfrac{d^2}{a^2}\right)^2 \\ +12\left(\dfrac{d^2}{a^2}\right)^3 + \left(\dfrac{d^2}{a^2}\right)^4 \end{array}\right)\left(1 - \frac{d^2}{a^2}\right)^{-10} - 1\right\} \qquad [1.58]$$

$$\mathrm{m} = \frac{a^2}{d^2}\left\{\left(1 + \frac{d^2}{a^2}\right)\left(1 - \frac{d^2}{a^2}\right)^{-4} - 1\right\} \qquad [1.59]$$

Figure 1.6 shows two curves illustrating the variations of our potential energy as a function of the ratio *d*/*a* for two values of the ratio d_0/a equal to 0.942 (part *a*) and 0.681 (part *b*). *A posteriori*, these two functions provide a justification: the first, for the approximation of the smoothed potential theory, as the potential energy is practically constant (part *a*), and the second, for the approximation of the 3D oscillator theory, with the potential energy showing a near-parabolic shape as a function of the distance (part *b*).

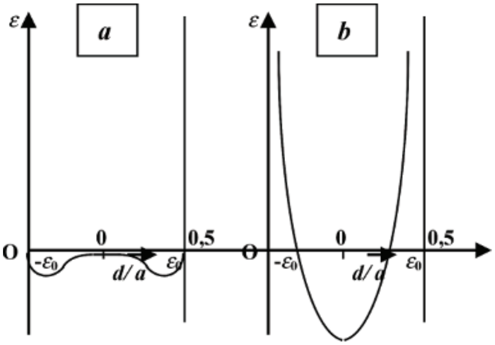

Figure 1.6. *Potential for interaction of a molecule in a liquid according to Lennard-Jones and Devonshire. a) for* $d_0/a = 0.942$*; b)* $d_0/a = 0.681$

By substituting expression [1.57] back into relation [1.53], the contribution of the translational motion to the canonical partition function can be written as:

$$Z_{C(t)} = \frac{1}{N!}\left[\frac{\mathrm{h}}{\left(2\pi m \mathrm{k_B} T\right)^{1/2}}\right]^{-3N}\left[2\pi N a^3 \int_0^{a/2} \exp\left(\frac{\langle \varepsilon(d)\rangle - \varepsilon(a)}{\mathrm{k_B}T}\right)\mathrm{d}\,x\right]^{N} \qquad [1.60]$$

According to Lennard-Jones and Devonshire, the integration limit in equation [1.60] is of no importance, because the greater part of the contribution is made by small distances, particularly where $d < a/2$.

If we set $x = d/a$, then the logarithm of the translational partition function is:

$$\begin{aligned}\ln Z_{C(t)} &= N \ln \frac{\left(2\pi m \mathrm{k_B} T\right)^{3/2}}{\mathrm{h}^3} + N \\ &+ N \frac{6\varepsilon_0\left[-2\left(\dfrac{d_0}{a}\right)^6 + \left(\dfrac{d_0}{a}\right)^{12}\right]}{\mathrm{k_B}T} + N\ln\left(2\pi a^3\right) + N\ln\left[\eta(\varepsilon_0, d_0)\right]\end{aligned} \qquad [1.61]$$

We have chosen $z = 12$, and $\eta(\varepsilon_0, d_0)$ denotes the function defined by:

$$\eta(\varepsilon_0, r_0) = \int_0^{1/2} x^{1/2} \exp\left[\frac{\varepsilon_0}{\mathrm{k_B} T} \left\{ \begin{matrix} \left(\dfrac{d_0}{a\gamma}\right)^{12} \mathrm{l}(x) \\ -2\left(\dfrac{d_0}{a\gamma}\right)^{6} \mathrm{m}(x) \end{matrix} \right\} \right] \mathrm{d}x \qquad [1.62]$$

d_0/a	$\dfrac{\varepsilon_0}{\mathrm{k_B}T} = -9$	$\dfrac{\varepsilon_0}{\mathrm{k_B}T} = -10$
0.942	0.00180	0.00161
0.918	0.00295	0.00269
0.891	0.00515	0.00478
0.858	0.00964	0.00916
0.818	0.01957	0.01920
0.765	0.0437	0.0445
0.730	0.0676	0.0700
0.681	0.1069	0.1125

Table 1.1. *Values of the function* $\eta(\varepsilon_0, d_0)$

The energy $\varepsilon(a)$ is given by:

$$\varepsilon(a) = \varepsilon_0 \left[-2\left(\frac{d_0}{a}\right)^6 + \left(\frac{d_0}{a}\right)^{12} \right] \qquad [1.63]$$

Table 1.1 gives a few values, which are easy to calculate automatically, for this function for two values of the ratio $\varepsilon_0/\mathrm{k_B}\mathrm{T}$ and different values of the ratio d_0/a.

Thus, if we accept the hypothesis of a cubic stack with centered faces, i.e. $\gamma = \sqrt{2}$, and if we know the molecular volume, the translational partition function contains only two parameters linked to the substance: d_0 and ε_0, which are the two parameters that play a part in the expression [A.3.44] (in Appendix 3) of the Lennard-Jones interaction potential.

In order to compare the result to other models and to experimental results, we need to deduce the expressions of the thermodynamic functions. From relation [A.3.48], we deduce the expression of the molecular Helmholtz energy function:

$$\frac{F}{N} = -\mathrm{k_B}T\ln\frac{\left(2\pi m\mathrm{k_B}T\right)^{3/2}}{\mathrm{h}^3} - \mathrm{k_B}T - \frac{6\varepsilon_0\left[-2\left(\frac{d_0}{a}\right)^6 + \left(\frac{d_0}{a}\right)^{12}\right]}{\mathrm{k_B}T} \qquad [1.64]$$
$$-\mathrm{k_B}T\ln\left(2\pi a^3\right) - \mathrm{k_B}T\ln z_{\mathrm{int}} - \mathrm{k_B}T\ln 2\sqrt{2}\pi\eta(\varepsilon_0,d_0)v_m$$

Here, z_{int} represents the contribution of all other internal motions of the molecule to the molecular partition function (rotations, vibrations, electronic and nuclear spin motions). For atomic liquids, this term can be taken as being equal to 1.

Based on the Helmholtz energy, it is easy to obtain the other thermodynamic functions such as:

$$PV_m = V_m\frac{\partial F}{\partial V} \qquad [1.65]$$

Thus:

$$PV_m = \mathrm{R}T\left\{\begin{array}{l} 1 + \frac{12\varepsilon(a)}{\mathrm{k_B}T}\left[2\left(\frac{d_0}{a\gamma}\right)^6 - 4\left(\frac{d_0}{a\gamma}\right)^{12}\right] \\ -48\frac{\varepsilon(a)}{2\mathrm{k_B}T}\left[\left(\frac{d_0}{a\gamma}\right)^{12}\frac{\eta_l(\varepsilon_0,d_0)}{\eta(\varepsilon_0,d_0)} - 2\left(\frac{d_0}{a\gamma}\right)^6\frac{\eta_m(\varepsilon_0,d_0)}{\eta(\varepsilon_0,d_0)}\right]\end{array}\right\} \qquad [1.66]$$

$\eta_l(\varepsilon_0,d_0)$ and $\eta_m(\varepsilon_0,d_0)$ being two functions, such as $\eta(\varepsilon_0,d_0)$, of the two variables d_0 and ε_0. They can be calculated numerically using the relations:

$$\eta_l(\varepsilon_0,r_0) = \int_0^{1/2} x^{1/2}\,\mathrm{l}(x)\exp\left[\frac{12\varepsilon_0}{\mathrm{k_B}T}\left\{\begin{array}{l}\left(\frac{d_0}{a\gamma}\right)^{12}\mathrm{l}(x) \\ -2\left(\frac{d_0}{a\gamma}\right)^6\mathrm{m}(x)\end{array}\right\}\right]\mathrm{d}x \qquad [1.67]$$

$$\eta_m(\varepsilon_0, r_0) = \int_0^{1/2} x^{1/2}\,\mathrm{m}(x) \exp\left[\frac{12\varepsilon_0}{\mathrm{k_B}T}\left\{\begin{matrix}\left(\dfrac{d_0}{a\gamma}\right)^{12} \mathrm{l}(x) \\ -2\left(\dfrac{d_0}{a\gamma}\right)^{6} \mathrm{m}(x)\end{matrix}\right\}\right] \mathrm{d}x \qquad [1.68]$$

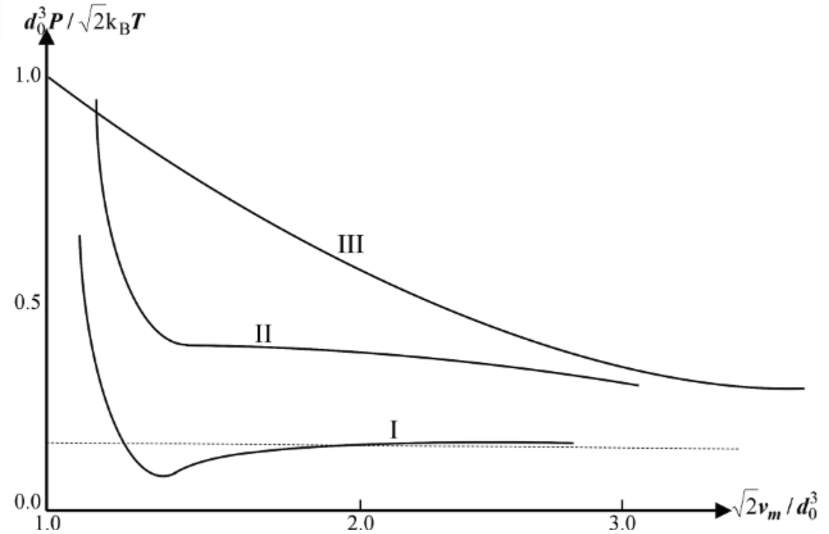

Figure 1.7. *Isotherms calculated using the Lennard-Jones and Devonshire model*

NOTE 1.2.– In expression [1.60], by comparison with the translational canonical partition function for a perfect gas (relation [A.3.26]), we can define the free volume of the molecules as:

$$\begin{aligned} v_f &= 2\pi a^3 \int_0^{1/2} \exp\left(\frac{\langle\varepsilon(d)\rangle - \varepsilon(a)}{\mathrm{k_B}T}\right) \mathrm{d}x \\ &= 2\pi\eta(\varepsilon_0, d_0)\gamma v_m = 2\sqrt{2}\pi\eta(\varepsilon_0, d_0) v_m \end{aligned} \qquad [1.69]$$

Figure 1.7 shows a few forms of isotherms in the representation $d_0^3 P / \sqrt{2}\mathrm{k_B}T$ as a function of $\sqrt{2}v_m / d_0^3$. Curve (III) is that of a perfect gas, curve (II) is obtained for $12\varepsilon_0 / \mathrm{k_B}T = -9$, and curve (I) for

$12\varepsilon_0 / \mathrm{k_B}T = -10$. It is noteworthy that curve (II) seems very similar to the critical isotherm which is given by:

$$T_c = -\frac{4\varepsilon_0}{3\mathrm{k_B}} \qquad [1.70]$$

The values obtained for certain liquids (see Table 1.2) show a satisfactory degree of accordance with their experimental values.

Substances	d_0 (Ä)	$-\varepsilon_0$ (10^{-22} joules/molecule)	T_c calculated	T_c observed
H_2	35.3	4.25	41	33
Ne	29.2	4.89	47	44.47
N_2	72.5	13.25	128	126
A	56.2	16.5	160	150.66

Table 1.2. *Values of the critical temperature, found experimentally and calculated by the Lennard-Jones and Devonshire model*

It is a fairly laborious task to rigorously calculate the critical volume, but from Figure 1.7, it seems we can choose the critical volume such that:

$$\frac{\sqrt{2}v_c}{d_0^3} = 2 \text{ so that } v_c = d_0^3\sqrt{2} \qquad [1.71]$$

We can see that this value is far too low. Indeed, it yields a value of 0.7 for $d_0^3 P / \sqrt{2}\mathrm{k_B}T$, instead of 0.3, which is the result found experimentally.

Thus, the Lennard-Jones and Devonshire cellular model can be used to calculate thermodynamic functions with only two adjustable parameters. In section 1.7, however, we shall demonstrate that the results obtained are very approximate, so there is a necessity to perfect the model. This was the purpose of the cellular and vacancies model developed by Ono and Eyring.

1.5. Cellular and vacancies model

Whilst it does represent real progress in relation to the previous two models, the Lennard-Jones and Devonshire model discussed above has a serious shortcoming–it is incapable of taking account of two dynamic properties of liquids: the phenomena of viscosity and self-diffusion. In order to take account of these properties, Ono [ONO 47] introduced the concept of vacancies, comparable to that which takes account of conductivity and diffusion in the solid phase. Ono considers that certain sites in the pseudo-lattice, or if you prefer, certain cells described in the above model, are not occupied, forming what we call vacancies. Thus, on average, over time, a molecule *i* will be surrounded by z_i first neighbors in accordance with:

$$z_i = y_i z \qquad [1.72]$$

y_i appears as the fraction of first-neighbor sites occupied around the molecule *i*. Therefore, y_i is a short-distance order index, whose value is zero when the central molecule *i* is surrounded only by holes (i.e. no molecules), and 1 if all the cells neighboring the central molecule are occupied (see section 3.2.1). Its spatial mean would be $<y_i>$, and would correspond to the mean value of the number of first neighbors $<z_i>$ determined by the first maximum of the radial distribution function demonstrated by X-ray diffraction. The number *z*, which is the coordination index, is in fact that maximum possible number of first neighbors, given by the chosen structure; that value is often taken to be equal to 12 for cubic cells with centered faces.

In order to take account, individually, of the environs of each molecule, we divide the liquid volume *V* into *L* cells ($L \geq N$) with respective volumes τ_1, τ_2 … τ_L. The configuration integral, which is expressed over the whole of the volume *V*, and plays a part in relation [1.53], will be replaced by a sum of partial integrals, each of which corresponds to an individual cell. Relation [1.53] then becomes:

$$Z_{C(t)} = \frac{1}{N!}\left[\frac{\mathrm{h}}{\left(2\pi m \mathrm{k_B} T\right)^{1/2}}\right]^{-3N} \sum_{l_1=1}^{L} \cdots \sum_{l_n=1}^{L} \int_{\tau_1} \cdots \int_{\tau_N} \exp\left(-\frac{\varepsilon\left(\omega^N\right)}{\mathrm{k_B}T}\right)\left(\mathrm{d}\,\omega\right)^N \qquad [1.73]$$

The sum contains L^N terms which correspond to L different cells, in relation to which the coordinates of the different molecules are expressed. Because each cell is supposed to be sufficiently small to contain at most one molecule, and sufficiently large so that the intermolecular forces are practically no longer felt beyond the immediately adjacent cells, the sums in expression [1.73] contain only $L!/(L\text{-}N)!$ non-null terms.

The energy $\varepsilon\left(\omega^N\right)$ in expression [1.71] will therefore be rewritten, instead of expression [1.54], in the form:

$$\varepsilon\left(\omega^N\right)=\sum_{i=1}^{N}\frac{z_i}{2}\varepsilon(a)+\sum_{i=1}^{N}\frac{z_i}{2}\left[\left\langle\varepsilon(d_i,y_i)\right\rangle-\varepsilon(a)\right] \quad [1.74]$$

The distance d_i is given, for each cell, by a relation similar to expression [1.55], namely:

$$d_i=\sqrt{r_i^2+a^2+2ar_i\cos\theta} \quad [1.75]$$

We use the notation v_c to denote the volume of a given cell, and for the cubic lattice with centered face, we have:

$$v_c=\frac{a^3}{\sqrt{2}} \quad [1.76]$$

Note that this cellular volume differs from the molecular volume $v_m = V/N$, because we no longer always have a molecule in each cell.

NOTE 1.3.– The volumes v_c and v_m have a known ratio, because we have:

$$\frac{v_c}{v_m}=\left\langle y_i\right\rangle=\frac{N}{L} \quad [1.77]$$

Hence, instead of relation [1.61], the translational canonical partition function is written as:

$$Z_{C(t)}=\frac{1}{N!}\left[\frac{\text{h}}{\left(2\pi m\text{k}_\text{B}T\right)^{1/2}}\right]^{-3N}\sum_{l_1=1}^{L}\ldots\sum_{l_N=1}^{L}\left[\prod_{i=1}^{N}\exp\left(-\frac{z_i\varepsilon(a)}{2\text{k}_\text{B}T}\right)\text{j}(y_i)\right] \quad [1.78]$$

The function j(y_i) is homogeneous with a volume. It is defined by:

$$\mathrm{j}(y_i)=\int_{\tau_i}4\pi r_i^2\left\{\exp\frac{-zy_i\left[\left\langle\varepsilon(d_i,y_i)\right\rangle\right]-\varepsilon(a)}{2\mathrm{k_B}T}\right\}\mathrm{d}r_i \tag{1.79}$$

If all the sites are occupied, $y_i = 1$ and j(y_i) is identified with the free volume logarithm v_f from relation [1.69]. If $y_i = 0$, then j(0) is the logarithm of the volume of the cell v_c.

We can see that the function j(y_i) is not a simple expression, and the various authors have been led to simplify it by a linear form of y_i as a function of the logarithm of v_f and v_c so as to satisfy the boundary values of $j(y_i)$. Thus, Ono proposed the expression:

$$\mathrm{j}(y_i)=y_i\ln\left(v_f\right)+\left(1-y_i\right)\ln v_c \tag{1.80}$$

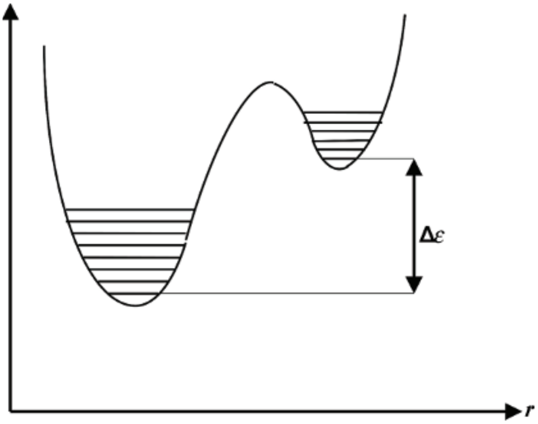

Figure 1.8. *Potential energy curve for a molecule occupying a more favorable position than a neighboring vacancy (from [REE 64])*

Eyring and his collaborators [REE 64] put forward the formula:

$$\mathrm{j}(y_i)=y_i\ln\left(v_f g_i\right)+\left(1-y_i\right)\ln v_c \tag{1.81}$$

Eyring's function differs from Ono's only by the introduction of a factor g, known as the *degeneration factor*, which is introduced because it is natural to suppose that, of all the places that are available, on average, for a molecule, some are more favorable than others, energetically speaking, simply because of the organization of the other molecules. This difference in energy between the most probable place and a less-probable near neighbor (see Figure 1.8) must be proportional to the interaction energy $z\varepsilon(a)/2$, and inversely proportional to the number of vacancies $n_h = z\left(1-\left\langle y_i\right\rangle\right)$. Thus, this energy difference would be of the form:

$$\Delta\varepsilon = \frac{kz\varepsilon(a)}{2n_h} = \frac{k\varepsilon(a)}{2\left(1-\left\langle y_i\right\rangle\right)} \qquad [1.82]$$

k is an adjustable constant of proportionality. Thus, the degeneration factor due to the vacancies present around a molecule would be written as:

$$\begin{aligned} g &= 1 + z\left(1-\left\langle y_i\right\rangle\right)\exp\left[\frac{\Delta\varepsilon}{\mathrm{k_B}T}\right] \\ &= 1 + z\left(1-\left\langle y_i\right\rangle\right)\exp\left[\frac{k\varepsilon(a)}{2\mathrm{k_B}T\left(1-\left\langle y_i\right\rangle\right)}\right] \end{aligned} \qquad [1.83]$$

The authors show that if we take account of relation [1.81], using the Bragg-Williams approximation ($\Delta\varepsilon = 0$ in g, see section 3.1.2) and Stirling's approximation [A.3.1], the translational canonical partition function [1.78] assumes the form:

$$\begin{aligned} \ln Z_{C(t)} = -3N\ln\frac{\mathrm{h}}{\left(2\pi m\mathrm{k_B}T\right)^{1/2}} + \frac{v_c N}{v_m}\Bigg\{\left[-\frac{z\varepsilon(a)}{2\mathrm{k_B}T}\right] + \ln\frac{v_f}{v_c} \\ + \ln\left[1+\frac{v_m - v_c}{v_m}\exp-\frac{kv_m\varepsilon(a)}{2(v_m\text{-}v_c)\mathrm{k_B}T}\right] \\ + N\ln v_m + \left(1-\frac{v_m}{v_c}\right)N\ln\left(1-\frac{v_c}{v_m}\right)\Bigg\} \end{aligned} \qquad [1.84]$$

Using this expression, the thermodynamic functions – particularly the Helmholtz energy – can be calculated.

1.6. Eyring's semi-microscopic formulation of the vacancy model

The expressions used by Eyring in the vacancy model become complicated and tricky to calculate numerically. In order to remedy this situation, Eyring and his collaborators [EYR 61] adapted the vacancy model to a semi-microscopic model, by replacing Lennard-Jones' interaction functions with macroscopic values, involving the molar volume of the solid $v^{0(sol)}$ at its melting point and that of the liquid $v^{0(liq)}$ at the temperature of study. Observing (except for a few very rare cases, one of which is water, which is not a non-associated liquid) a significant increase (around a twofold increase) in the molar volume upon transitioning from the solid state to the liquid state, the authors model a liquid as being a two-component solution:

– molecules, which behave like a molecule in a solid, i.e. three vibrational degrees of freedom. This is the model of the short-distance lattice aspect;

– vacancies, which behave like a gas, and therefore have three translational degrees of freedom, which we shall suppose to be perfect, with non-localized objects that are free to move around, which will create disorder over a long distance and mobility of the species.

Of course, the movement of a vacancy is, in fact, the movement of a molecule neighboring that vacancy.

Solids, just below their melting point, are assumed to contain no vacancies. If there are any, they are few in number in relation to the molecules. In a liquid, on the other hand, the number of vacancies is of the same order of magnitude as the number of molecules. If N denotes the number of molecules behaving like a solid, the number of vacancies would be:

$$N_L = N\frac{v^{0(liq)} - v^{0(sol)}}{v^{0(sol)}} \qquad [1.85]$$

Thus, the total number of cells would be:

$$N_c = N_L + N = N\frac{v^{0(liq)} - v^{0(sol)}}{v^{0(sol)}} \quad [1.86]$$

Hence, the fraction of sites with molecules would be:

$$x_s = \frac{N}{N_c} = \frac{v^{0(sol)}}{v^{0(liq)}} \quad [1.87]$$

and the fraction of sites with vacancies would be:

$$x_L = \frac{N_L}{N_c} = \frac{v^{0(liq)} - v^{0(sol)}}{v^{0(sol)}} \quad [1.88]$$

The mean number of vacancies neighboring a molecule (z is the coordination index of the lattice) would be:

$$\langle n_L \rangle = z\frac{x_L}{x_s} = z\frac{v^{0(sol)}}{v^{0(liq)}} \quad [1.89]$$

By applying relation [A.3.36] to both components of the solution, we can calculate the canonical partition function on the basis of that of the localized molecules and non-localized vacancies, so that:

$$Z_C = Z_{C(s)}.Z_{C(L)} \quad [1.90]$$

As the vacancies behave like a perfect gas with three translational degrees of freedom, we have:

$$Z_{C(L)} = \left\{\left[\frac{\mathrm{h}}{\left(2\pi m \mathrm{k_B} T\right)^{1/2}}\right]^{-3}\left(v^{0(liq)} - v^{0(sol)}\right)\right\}^{N\frac{v^{0(liq)} - v^{0(sol)}}{v^{0(sol)}}} \left\{\left(N\frac{v^{0(liq)} - v^{0(sol)}}{v^{0(liq)}}\right)!\right\}^{-1} \quad [1.91]$$

For molecules which behave like a solid, with three vibrational degrees of freedom, if we ignore the residual vibration, we have:

$$Z_{C(s)} = \frac{g}{\left[1 - \exp\left(-\frac{\mathrm{h}\nu}{\mathrm{k_B}T}\right)\right]^3} \qquad [1.92]$$

The degeneration coefficient is calculated in a similar manner to that used to obtain relation [1.85]. Its value is:

$$g = 1 + n\exp\left[-\frac{\Delta\varepsilon}{\mathrm{k_B}T}\right] \qquad [1.93]$$

If $\Delta_S U$ is the Helmholtz energy of sublimation of the solid, the variation in energy $\Delta\varepsilon$ (Figure 1.8) will be proportional to the sublimation energy and inversely proportional to the number of vacancies N_L. We can write this in a similar manner to expression [1.82]:

$$\Delta\varepsilon = \frac{k\Delta_s U v^{0(sol)}}{v^{0(liq)} - v^{0(sol)}} \qquad [1.94]$$

The partition function of the molecules with solid behavior would therefore be:

$$Z_{C(s)} = \left\{ \frac{\exp\left(\frac{\Delta_s U}{\mathrm{R}T}\right)}{\left[1 - \exp\left(-\frac{\mathrm{h}\nu}{\mathrm{k_B}T}\right)\right]^3} \left(1 + \langle n \rangle \frac{v^{0(liq)} - v^{0(sol)}}{v^{0(sol)}} \exp - \frac{k\Delta_s U v^{0(sol)}}{\mathrm{R}T\left(v^{0(liq)} - v^{0(sol)}\right)} \right) \right\}^{\frac{Nv^{0(sol)}}{v^{0(liq)}}} \qquad [1.95]$$

Using expressions [1.90], [1.91] and [1.95] for the overall partition function, and after application of Stirling's approximation, we find:

$$\begin{aligned}\ln Z_C = \frac{N v^{0(sol)}}{v^{0(liq)}} & \left\{ \begin{array}{l} \dfrac{\Delta_s U}{\mathrm{R}T} - 3\ln\left[1-\exp\left(-\dfrac{\mathrm{h}\nu}{\mathrm{k_B}T}\right)\right] + \\ \ln\left(1 + z\dfrac{v^{0(liq)} - v^{0(sol)}}{v^{0(liq)}}\exp - \dfrac{k\Delta_s U v^{0(sol)}}{\mathrm{R}T\left(v^{0(liq)} - v^{0(sol)}\right)}\right) \end{array} \right\} \\ & + \frac{N\left(v^{0(liq)} - v^{0(sol)}\right)}{v^{0(liq)}}\left[-3\ln\frac{\mathrm{h}}{\left(2\pi m \mathrm{k_B} T\right)^{1/2}} + \ln\frac{e v^{0(liq)}}{N}\right]\end{aligned} \qquad [1.96]$$

We can see that the canonical partition function, and therefore all the thermodynamic functions (particularly the Helmholtz energy) depend only on the single adjustable parameter *k* defined in expression [1.94]. Hence, this model is a simple and powerful tool.

The model we have just looked at is that which applies to atomic liquids, such as argon, for instance. Eyring and his collaborators carried out parallel tests, applied to the cases of molten salts and liquid metals.

NOTE 1.4.– It is worth noting that Eyring's model, for the partition function (relation [1.90]) is tantamount to mixing Guggenheim's (section 1.3.1) and Mie's (section 1.3.2) models. These models gave a good account of the properties of liquids respectively in the vicinity of a gaseous state and of a solid state.

1.7. Comparison between the different microscopic models and experimental results

A variety of comparisons have been offered by the different creators of models: comparisons between a model and the experimental results, comparisons between different models, and comparisons between results produced by a model and those produced by simulation calculations. Indeed, the calculation methods used for statistic simulation lend themselves very well to this type of problem. Examples include the static Monte Carlo method, based on equation [1.3], or the molecular dynamics method, based on the fundamental law of dynamics (see Appendix 1).

In terms of comparison with experimental values, we shall give the example of the variation in heat capacity at constant volume as a function of the temperature calculated by Eyring's semi-microscopic method. Remember that it is a cellular model including vacancies and a degeneration coefficient (see section 1.6). Figure 1.9 illustrates such a comparison and exhibits good accordance between the results obtained by the model and the experimental results.

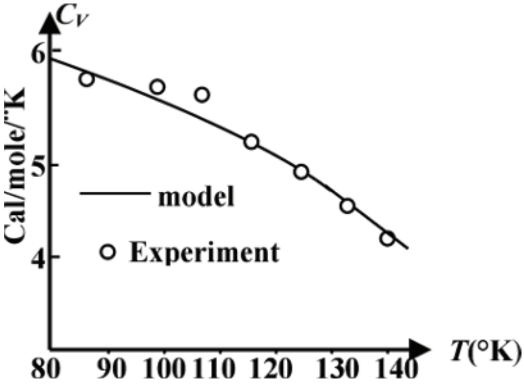

Figure 1.9. *Comparison between the observed values of the heat capacity at constant volume and those calculated using the cellular and vacancies model by Eyring et al. [EYR 61]*

Figure 1.10 shows the comparison of the result of the same model of the radial distribution function curve for argon at a temperature of 84.4K, against the experimental result. Once again, we see excellent accordance.

Certain comparisons are made between the measured values and those calculated by a model, for the critical values – particularly the critical temperature and critical pressure, using the conditions:

$$\left(\frac{\partial F}{\partial V}\right)_T = -P \qquad \left(\frac{\partial P}{\partial V}\right)_T = 0 \qquad \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 \qquad [1.97]$$

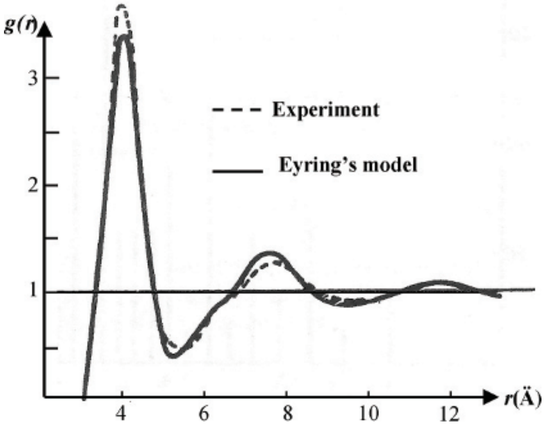

Figure 1.10. *Comparison between the experimental value and that calculated by Eyring's model for the radial distribution function of Argon at 84.4K (data from [YOO 81])*

Substance	T_c (°K)		P_c (atm)	
	Calculated	Observed	Calculated	Observed
Neon	55.41	44.47	37.65	26.86
Argon	154.44	150.66	58.72	48.00
Krypton	208.33	210.60	69.68	54.24
Xenon	287.80	289.80	74.89	58.20

Table 1.3. *Comparison of the observed values and those calculated by the Eyring model, for the temperature and the critical pressure (data from [EYR 58])*

Certain data appear in Table 1.2 for Lennard-Jones and Devonshire's model (see section 1.4). Others are given for the solids of rare gases in Table 1.3, and pertain to Eyring's model (see section 1.5).

Note that both models yield satisfactory results on this point. However, it is important to apply the comparison to several types of results. For example, Figure 1.11 shows that, for the representation of the distribution function, Lennard-Jones and Devonshire's model, Eyring's model and the calculations performed by numerical simulation are very similar. Meanwhile, Figure 1.12, which gives the variation of the compressibility coefficient as a function of a reduced volume, illustrates the significant behavioral difference between the molecular dynamics simulation and Eyring's model, on the one hand, and Lennard-Jones/Devonshire's, Guggenheim's (see section 1.3.1) and Mie’s model (see section 1.3.2), on the other. It seems that the important point which divides Eyring’s model from that of Lennard-Jones and Devonshire is more the introduction of the degeneration coefficient than the variability of the number of molecules that are near neighbors of a given molecule (z_i).

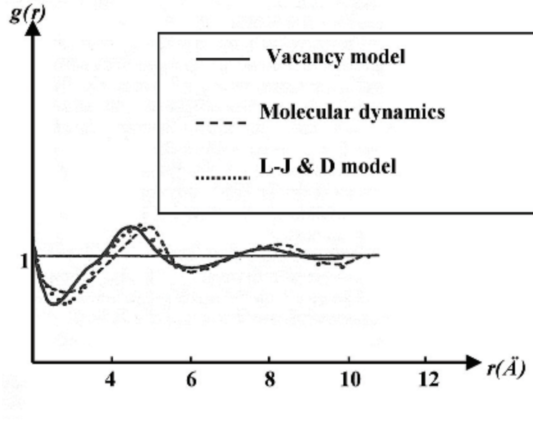

Figure 1.11. *Comparison of the curve of the radial distribution function between the calculations of molecular dynamics and different models (according to [YOO 81])*

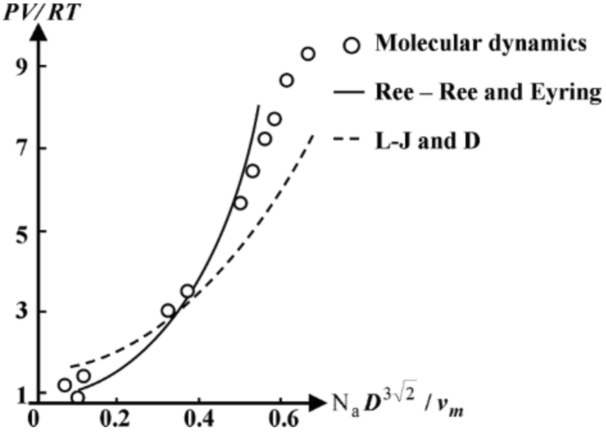

Figure 1.12. *Comparison of the results obtained on the compressibility factor (data from [REE 64])*

Thus, we can see that it is important to examine the validity of a model by comparing several results produced by that model. Additionally, a good model of the structure of liquids must also satisfy the interpretation of properties other than the mere thermodynamic values that are of interest to us here, e.g. surface tension, viscosity and self-diffusion. The major advantage of Eyring’s cellular and vacancy model with a degeneration coefficient is that it also takes account of the dynamic properties of liquids.