5. MEAN FIELD APPROXIMATIONS IN STATISTICAL MECHANICS

5.1 Introduction

The perfectly general formalism of the equilibrium ensembles provides a link between molecular-level information and thermodynamic properties. In practice, however, an exact analytical solution of this formalism is impossible for all but the simplest Hamiltonians (*e.g.*, the ideal gas Hamiltonian examined in Section 4.7). A major source of difficulty in deriving analytical solutions to the ensemble formalism stems from the need to sum or integrate over a very large number of microstates or configurations in calculating partition functions or configurational integrals [compare Eqs. (4.16), (4.38)]. *Approximations* are absolutely necessary to arrive at closed-form solutions for microscopic models that are realistic enough to be useful for addressing the properties of materials.

Mean field approximations neglect correlations between different parts of a material system at some level, and thus obviate the need to consider a multitude of configurations in deriving the system thermodynamics. The closed- form solutions obtained on the basis of such approximations may be satisfactory over relatively wide ranges of conditions. Clearly, however, mean field approximations are bound to break down when fluctuations in properties as the system changes configuration become large relative to the average values of these properties and thus dominate the system thermodynamics. As suggested

by our analysis of energy fluctuations in the canonical ensemble (section 4.5.2), fluctuations become large when the system is near its limit of stability with respect to a phase transition; under such conditions, the performance of mean field theories is expected to be poor.

In constructing a mean field approximation one may follow one of several strategies. A common strategy is to define a variable, or *order parameter*, that provides a collective description of configuration. Examples of such variables are the magnetization in the study of the Curie point transition of ferromagnetic systems; the density difference between two phases in the study of phase equilibria of isotropic single component systems; and the concentration difference between two phases in the study of phase splitting in two-component systems. An expression is written for the Helmholtz or Gibbs energy in terms of the order parameter, and this expression is minimized to impose the condition of thermodynamic equilibrium (Landau theory of phase transitions [Lifshitz and Pitaevskii 1980]) As the system goes through a phase transition, the order parameter changes from zero to nonzero values (*symmetry breaking*). An alternative strategy starts by approximating a system of interacting particles by an "equivalent" system of noninteracting particles subject to an external field. The effects of other particles on a given particle enters through this field, which depends on the order parameter. For example, a spin in the Ising model of a ferromagnet is envisioned as immersed in a field generated by the mean magnetization of surrounding spins, with which it interacts. The thermodynamics of the system is derived by imposing the condition that this "*mean field*" be *self consistent*, *i.e.*, that the response (contribution to the order parameter) it elicits from a

particle be consistent with the magnitude of the order parameter that shapes its value. In the Ising model, for example, self-consistency demands that the average magnetic moment of a spin immersed in the mean magnetic field generated by surrounding spins must equal the magnetization that collectively represents the state of the surrounding spins.

Mean field approximations have played an important role in the development of theories for phase transitions and critical phenomena. The modern theory of the renormalization group [Wilson and Kogut 1974] provides a more robust and reliable framework for treating these phenomena. In this respect, and from a physicist's point of view, mean field theory has been superseded. Nevertheless, when used judiciously, mean field approaches can still be quite helpful in attacking complex problems of engineering interest in a tractable way. As already mentioned, a serious fault of mean field theories is their neglect of spatial fluctuations of the order parameter that may be correlated over large distances. The importance of this omission depends on the spatial dimensionality of the system under investigation. In systems of low dimensionality (1-d, 2-d) mean field predictions for phase behavior are frequently qualitatively wrong.

One should be aware that the term "mean field" is used rather loosely to designate a spectrum of approaches, ranging from quite crude to very sophisticated. This is not surprising; correlations in a system can be neglected at several levels. It is perhaps best not to use the term "mean field" at all, but rather refer to the particular approximation employed by name (*e.g.*, Bragg-Williams approximation of random mixing in lattice fluid

models; Guggenheim quasichemical approximation for the estimation of local composition in fluid mixtures; Flory approximation for the estimation of the configurational entropy of polymer chain systems; Debye-Hückel approximation for the distribution of the atmosphere of counterions around a central ion, *etc.*)

In this discussion we will present two simple examples of mean field approaches. The first concerns the application of the *Bragg-Williams* approximation on a lattice to derive a simple regular solution model for binary alloys or liquid mixtures; the Guggenheim *quasichemical* approximation will also be briefly discussed as providing a higher degree of refinement for the same problem. The second example concerns the derivation of the *van der Waals* equation of state.

5.2 Simple Model of Binary Mixture Thermodynamics: Bragg-Williams and Quasichemical Approximations

5.2.1 Lattice Model of an Incompressible Binary Mixture

Simple lattice models are useful for describing the mixing thermodynamics of metals forming substitutional solid solutions. The same types of models provide a conceptual framework for studying the mixing properties of liquids, although, of course, a lattice picture is much less justified in the liquid state. Lattices are convenient because they allow easy enumeration of configurations. Insofar as momentum contributions to the

partition function remain the same in the pure and the mixed states, the statistical mechanical analysis can be conducted entirely in configuration space. Thus, in this section we will make no distinction between "partition function" and "configurational sum" or integral.

Consider a lattice containing a total of N sites. Each site can accommodate one A or one B molecule. Multiple occupancy of a site by molecules is prohibited by short-range repulsive interactions. The lattice, whose coordination number will be denoted by z, is assumed fully occupied. Molecules occupying adjacent sites in the lattice interact through short- range attractive forces, but there are no interactions over larger distances. The characteristic energies of nearest-neighbor attractive interactions per pair of interacting molecules are w_{AA}, w_{BB}, and w_{AB}; all three are negative quantities (see Fig.5.1).

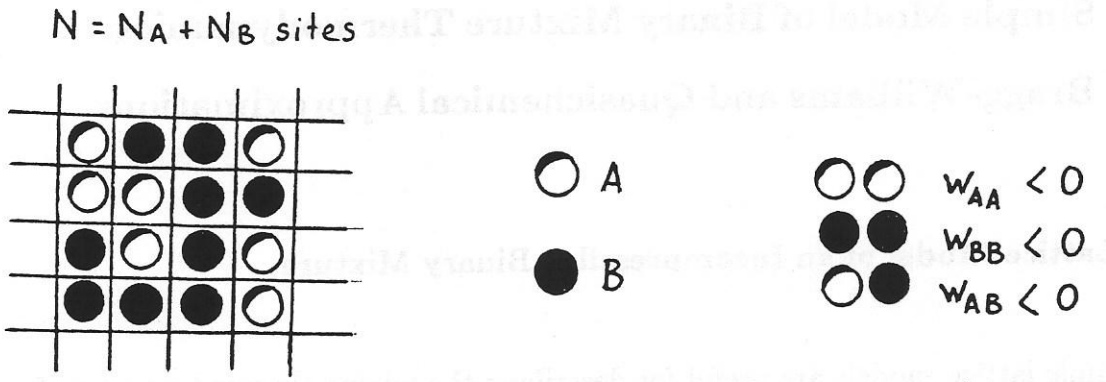

Figure 5.1 Schematic representation of simple lattice model of a binary mixture.

The numbers of A and B molecules in the lattice are denoted by N_A, N_B, respectively. By the full occupancy requirement, one has

$$N_A + N_B = N \tag{5.1}$$

The mole fractions $x_A = N_A/N$ and $x_B = N_B/N$ are intensive descriptors of composition.

The objective of this analysis will be to derive the thermodynamics of mixing of A and B on the basis of this simple lattice model. From macroscopic thermodynamics we know that the excess molar Gibbs energy function $g^E = g^E(T, x_A)$ is all we need for this purpose. If we know g^E, we can extract activity coefficients for the two components, formulate phase equilibrium problems, and construct the phase diagram of the binary system. Note that the lattice model we employ here allows no volume change upon mixing: $\Delta V_{mix} = V^E = 0$. As a consequence, the mixing thermodynamics will be pressure-independent, and g^E can be identified with the excess molar Helmholtz energy a^E:

$$a^E = g^E \text{ for any } T, x_A \tag{5.2}$$

In this analysis we choose to study the lattice model under constant N_A, N_B, and T. By Eq. (5.1), the total number of lattice sites is fixed. We thus have a system of fixed temperature, spatial extent, and numbers of molecules of all species involved; in other words, our analysis is conducted in the *canonical ensemble.*

Consider the lattice model in a given configuration (distribution of A and B molecules among the sites). Let N_{AA}, N_{BB}, and N_{AB} be the total numbers of nearest-neighbor AA, BB, and AB pairs in this configuration. These numbers are related to one another and to the numbers of sites N_A and N_B through simple counting relations. To appreciate this, consider that every A site in the lattice is connected by a bond to all its nearest-neighbor sites (Figure 5.2). The total number of bonds drawn in this way will be $z\,N_A$. When the connection exercise is completed, each nearest-neighbor AA pair will

carry two bonds; each nearest-neighbor AB pair will carry one bond; and no nearest-neighbor BB pair will carry a bond. Consequently,

$$z\,N_A = 2\,N_{AA} + N_{AB} \tag{5.3a}$$

and, by repeating the exercise around B molecules,

$$z\,N_B = 2\,N_{BB} + N_{AB} \tag{5.3b}$$

In view of Eqs. (5.3), N_{AA} and N_{BB} can be expressed as functions of N_A, N_B, and N_{AB}.

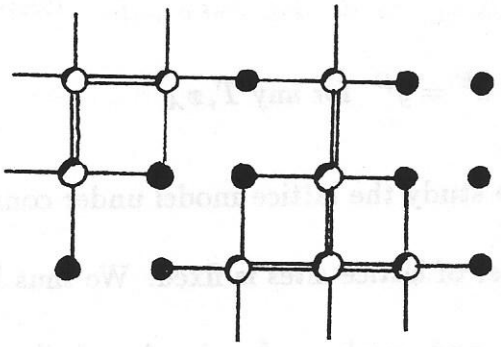

Figure 5.2 For the derivation of counting relations involving the numbers of nearest neighbor AA, BB, and AB pairs

Using Eqs. (5.3), we can express the potential energy of the considered configuration as

$$E = N_{AA}\,w_{AA} + N_{BB}\,w_{BB} + N_{AB}\,w_{AB} =$$

$$\frac{z\,N_A}{2}\,w_{AA} + \frac{z\,N_B}{2}\,w_{BB} + N_{AB}\left(w_{AB} - \frac{1}{2}w_{AA} - \frac{1}{2}w_{BB}\right) =$$

$$E_A + E_B + \frac{1}{z}N_{AB}\,w \tag{5.4}$$

where $E_A = \frac{z N_A}{2} w_{AA}$ is the total potential energy of a pure A system consisting of N_A molecules, and similarly for pure B. (The division by 2 is needed to avoid doublecounting of ineractions in the pure component lattices). The quantity

$$w = z \left(w_{AB} - \frac{w_{AA}}{2} - \frac{w_{BB}}{2} \right)$$

is called *interchange energy*. The physical meaning of this quantity can be explained by considering the simple process of Fig. 5.3. On the left hand side of the figure are a pure lattice of A molecules and a pure lattice of B molecules. One molecule is taken from each lattice and placed within the other lattice. The total potential energy change *per exchanged atom* associated with this process is

$$\frac{2 z w_{AB} - z w_{AA} - z w_{BB}}{2} = w$$

When $w < 0$, interactions between unlike molecules are more favorable than interactions between like molecules, and *negative* deviations from ideal solution behavior are expected. When $w > 0$, interactions between unlike molecules are less favorable than those between like molecules, and *positive* deviations from ideal solution behavior are expected.

When attractive interactions are due to London dispersion forces, an interesting relationship can be established between the interchange energy w and the cohesive energy densities of pure A and pure B. For London dispersion forces, the *Lorentz-Berthelot rule* is often used to relate the characteristic interaction energies between like and unlike molecules:

$$|w_{AB}| \simeq (|w_{AA}|\,|w_{BB}|)^{\frac{1}{2}}$$

Using the symbol v^* for the volume of a lattice site, and substituting the Lorentz-Berthelot rule into the definition of the interchange energy, we obtain

$$w = \frac{z}{2}\left(|w_{AA}|^{\frac{1}{2}} - |w_{BB}|^{\frac{1}{2}}\right)^2 = v^*\left[\left(\frac{z}{2v^*}|w_{AA}|\right)^{\frac{1}{2}} - \left(\frac{z}{2v^*}|w_{BB}|\right)^{\frac{1}{2}}\right]^2 =$$

$$v^*\left[\left(\frac{|E_A|}{N_A v^*}\right)^{\frac{1}{2}} - \left(\frac{|E_B|}{N_B v^*}\right)^{\frac{1}{2}}\right]^2 = v^*\left[\left(\frac{|E_A|}{V_A}\right)^{\frac{1}{2}} - \left(\frac{|E_B|}{V_B}\right)^{\frac{1}{2}}\right]^2 , \text{ or}$$

$$w = v^*(\delta_A - \delta_B)^2$$

where $|E_I|/V_I$ is the cohesive energy density of pure species I, and δ_I is its Hildebrand solubility parameter.

Figure 5.3 For the explanation of the interchange energy w

In view of Eq. (5.4), the canonical partition function of the mixed system is

$$Q(N_A, N_B, T) = \sum_{all\ configs} exp(-\beta E_{config}) =$$

$$\sum_{N_{AB}} g(N_A, N_B, N_{AB})\ exp\left[-\beta\left(E_A + E_B + \frac{N_{AB}}{z}w\right)\right] \qquad (5.5)$$

where $g(N_A, N_B, N_{AB})$ stands for the number of system configurations containing exactly N_{AB} nearest-neighbor pairs of unlike molecules. In the sum on the right-hand side of Eq. (5.5), configurations are grouped by the number of nearest-neighbor pairs of unlike molecules they contain. This is useful because configurations with the same N_{AB} are isoenergetic, and therefore have the same Boltzmann factor.

5.2.2 Bragg-Williams Approximation

Eq. (5.5) for the partition function of the mixture is exact. If $g(N_A, N_B, N_{AB})$ were known explicitly as a function of N_{AB}, performing the summation over all configurations in Eq. (5.5) would yield the system thermodynamics. An analytical expression for $g(N_A, N_B, N_{AB})$ is not available, however. Our goal is to introduce a mean-field approximation and thus obviate the need to consider all possible configurations in Eq. (5.5).

Mean Field Approximation At equilibrium, far from the limit of stability of the considered mixed phase, we expect that N_{AB} will be strongly peaked around its average value, $\langle N_{AB} \rangle$. We choose to substitute N_{AB} by this average value in *all* Boltzmann factors appearing in Eq. (5.5):

$$Q_{MF}(N_A, N_B, T) = exp\left[-\beta\left(E_A + E_B + \frac{\langle N_{AB} \rangle}{z} w\right)\right] \sum_{N_{AB}} g(N_A, N_B, N_{AB}) \qquad (5.6)$$

Note that this approximation involves *throwing away fluctuations* in N_{AB}. Now, $\sum_{N_{AB}} g(N_A, N_B, N_{AB})$ is the *total* number of lattice configurations of N_A A-molecules and

N_B B-molecules on $N_A + N_B = N$ lattice sites:

$$\sum_{N_{AB}} g(N_A, N_B, N_{AB}) = \frac{N!}{N_A! N_B!} \tag{5.7}$$

Note that molecules of the same type have been treated as *indistinguishable* in writing Eq. (5.7). Combining Eqs. (5.6) and (5.7),

$$Q_{MF}(N_A, N_B, T) = \frac{N!}{N_A! N_B!} \, exp\left[-\beta\left(E_A + E_B + \frac{\langle N_{AB}\rangle}{z} w\right)\right] \tag{5.8}$$

To complete the formulation, we need an expression for $\langle N_{AB}\rangle$. To this end, we introduce the following simplification:

Bragg-Williams approximation of random mixing. "There is no short-range order apart from that which follows from long-range order".

$$\langle N_{AB}\rangle = N^*_{AB} \equiv N_A \, z \left(\frac{N_B}{N}\right) \tag{5.9}$$

In Eq. (5.9), N^*_{AB} denotes the number of unlike nearest neighbor pairs in a "random mixture", in which AA, BB, and AB interactions are identical ($w = 0$). In such a mixture, one expects that the local composition around a given molecule will be no different than the overall composition. If we focus our attention on the environment of an A molecule, the fraction of its nearest-neighbor sites occupied by B molecules will equal the mole fraction of B molecules in the lattice, N_B/N. Thus, N^*_{AB} equals the number of A molecules times the lattice coordination number times the mole fraction of B molecules. Equating the quantity $\langle N_{AB}\rangle$ (descriptive of the local conposition or "short-range order" of the system) with N^*_{AB} (which is dictated by the overall composition or

"long-range order") is the essence of the Bragg-Williams approximation. In reality, the disparities among interactions between similar and dissimilar molecules will cause the local composition to deviate from that of the random mixture. In particular, one expects that $\langle N_{AB} \rangle > N^*_{AB}$ when $w < 0$ and $\langle N_{AB} \rangle < N^*_{AB}$ when $w > 0$. Introduction of the Bragg-Williams approximation in Eq. (5.8) leads to

$$Q_{MF}(N_A, N_B, T) = \frac{N!}{N_A!\, N_B!}\; exp\left[-\beta\left(E_A + E_B + \frac{N_A\, N_B}{N}\, w\right)\right] \tag{5.10}$$

The partition function has now been expressed entirely in terms of known quantities, and we are ready to extract the thermodynamics of the mixture in the mean field approximation. By equation (4.18), and invoking Stirling's approximation,

$$A(N_A, N_B, T) = -\frac{1}{\beta}\, \ln Q_{MF}(N_A, N_B, T) =$$

$$k_B\, T\left[N_A \ln\left(\frac{N_A}{N}\right) + N_B \ln\left(\frac{N_B}{N}\right)\right] + E_A + E_B + \frac{N_A\, N_B}{N}\, w \tag{5.11}$$

The Helmholtz energy of mixing is

$$\Delta A_{mix}(N_A, N_B, T) = A(N_A, N_B, T) - A_A(N_A, T) - A_B(N_B, T)$$

The pure component Helmholtz energies A_A and A_B are the same as the pure component potential energies E_A and E_B; this is because molecules of the same type are considered as indistinguishable in the lattice formulation, so each pure component lattice can exist only in one configuration. Substituting $A(N_A, N_B, T)$ from Eq. (5.11), we obtain

$$\frac{\Delta A_{mix}(N_A, N_B, T)}{N} = k_B\, T\left[\frac{N_A}{N} \ln\left(\frac{N_A}{N}\right) + \frac{N_B}{N} \ln\left(\frac{N_B}{N}\right)\right] + \frac{N_A}{N}\, \frac{N_B}{N}\, w$$

which leads to the following expression for the molar Helmholtz energy of mixing:

$$\Delta a_{mix}(x_A, T) = RT\,(x_A \ln x_A + x_B \ln x_B) + N_{Avo} w\, x_A\, x_B \tag{5.12}$$

or, taking into account Eq. (5.2), and setting $w' = N_{Avo}\, w$,

$$a^E(x_A, T) \equiv g^E(x_A, T) = w'\, x_A\, x_B \tag{5.13}$$

The Bragg-Williams solution to the lattice mixture problem is none else than the two-suffix Margules solution model [Prausnitz *et al.* 1986]. Note that, for this solution model, the excess Gibbs energy is purely enthalpic:

$$h^E(x_A, T) = \left(\frac{\partial(g^E/T)}{\partial(1/T)}\right)_{x_A} = w'\, x_A\, x_B \quad \text{and, consequently, } s^E = \frac{h^E - g^E}{T} = 0 \tag{5.14}$$

This is to be expected, as the configurational distribution of the system was assumed identical to that of a random mixture. The fact that $s^E = 0, v^E = 0$ makes the Bragg-Williams mean field lattice model a *regular solution* model. The activity coefficients derived from it are given by

$$\ln \gamma_A = \frac{w}{k_B\, T}\, x_B^2, \quad \ln \gamma_B = \frac{w}{k_B\, T}\, x_A^2 \tag{5.15}$$

Some information on the ability of this model to fit experimental data from real alloys is presented in [Lupis 1983].

For $w > 0$ the Bragg-Williams solution predicts splitting into two phases below an upper consolute temperature of $T_c = \dfrac{w}{2\, k_B}$. The binodal curve calculated on the basis of the Bragg-Williams approximation is shown in Figure 5.4.

An exact analytical solution of the binary mixture lattice model is possible in one and two dimensions, but not in three dimensions. The model can be mapped directly onto the Ising model of ferromagnetism, which has been studied heavily within the framework of modern theory of phase transitions and critical phenomena. In three dimensions Padé approximant expressions have been developed to describe the "exact" results obtained from simulation [Scesney 1970]. A plot of the binodal, based on such a description of the exact solution for a cubic lattice, is shown in Fig. 5.4 along with the Bragg-Williams result. Although the qualitative predictions of the Bragg-Williams solution are correct, its quantitative agreement with the exact results is not very good, especially in the vicinity of the critical point. The Bragg-Williams solution overestimates the critical point and the extent of the immiscibility region. The Bragg-Williams binodal is clearly more pointed than the exact binodal, whose flattened shape around the critical point is described by a universal "critical exponent". The departure of the Bragg-Williams solution from the exact solution is a consequence of its neglect of configurational fluctuations, which exert a profound influence on the thermodynamics around the critical point. We now briefly examine an improved mean field approximation that disregards fluctuations at a higher level than the Bragg- Williams and thus provides a more satisfactory representation of the exact results.

5.2.3 The Quasichemical Approximation

The development of this improved mean field approximation for liquid mixtures is due to Guggenheim. The same approximation applied to the Ising model of ferromag-

nets is known as *Bethe-Peierls* approximation. As opposed to the Bragg-Williams, this approximation introduces local composition effects in describing the configuration of the lattice system.

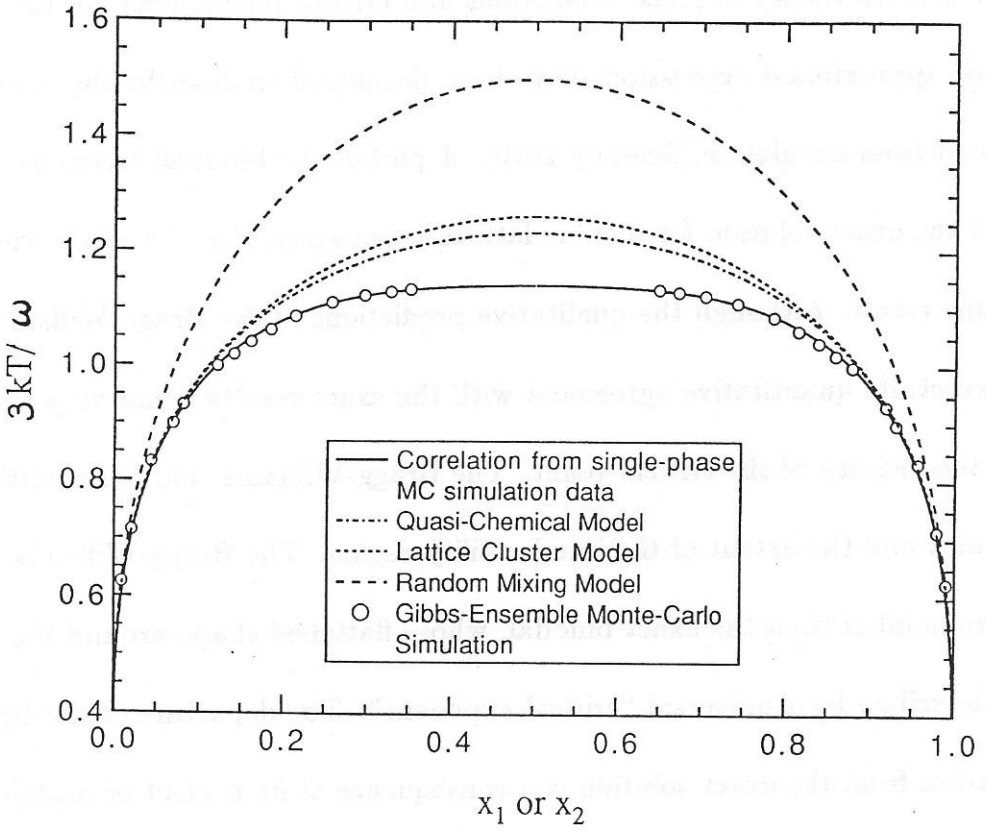

Figure 5.4 Binodal curve for a binary mixture lattice model with interchange energy w. The exact result from Monte Carlo simulations of the simple cubic lattice ($z = 6$) [Lambert, Soane, and Prausnitz 1992] is compared with estimates based on the Bragg-Williams random mixing approximation and on the Guggenheim quasichemical approximation. A prediction from the lattice cluster approach of Freed is also shown. The abscissa is mole fraction of species A; the ordinate is temperature, in units of $w/(3\ k_B)$.

Our starting point is Eq. (5.5) for the partition function. In the thermodynamic limit, far from regions of instability, it is expected that one of the terms in the summation of Eq. (5.5), corresponding to a particular value of N_{AB}, will be dominant, its value governing the behavior of the entire partition function. The basic strategy followed in the quasichemical approach is the following: *(i)* Develop an approximate expression for $g(N_A, N_B, N_{AB})$ as a function of N_{AB}; *(ii)* Using this expression, calculate the value $\langle N_{AB} \rangle$ that maximizes the term $g(N_A, n_B, N_{AB})\ exp[-\beta\,(E_A + E_B + N_{AB}/z\ w)]$, and determine the maximum value of that term; *(iii)* Substitute the partition function by its maximum term and derive from it the mixture thermodynamics (*maximum term approximation*).

There are many ways of formulating the quasichemical approximation to the quantity $g(N_A, N_B, N_{AB})$. One way is to consider the system as consisting of randomly mixed AA, BB, AB, and BA pairs. The quantity $g(N_A, N_B, N_{AB})$ is written as

$$g(N_A, N_B, N_{AB}) = h(N_A, N_B)\ \frac{(N_{AA} + N_{BB} + N_{AB})!}{N_{AA}!\, N_{BB}!\, (\frac{N_{AB}}{2})!\, (\frac{N_{AB}}{2})!} =$$

$$h(N_A, N_B)\ \frac{\left[\frac{1}{2} z\,(N_A + N_B)\right]!}{N_{AA}!\, N_{BB}!\, \left[(\frac{N_{AB}}{2})!\right]^2} \tag{5.16}$$

The factor $h(N_A, N_B)$ is assumed dependent on the numbers of molecules but *not* on the numbers of pairs, which appear exclusively in the combinatorial terms of Eq. (5.16). The counting relations, Eq. (5.3), have been used in the last transformation.

Whereas random mixing of *molecules* was postulated in the Bragg-Williams approximation, random mixing of *pairs* is assumed in Eq. (5.16). Thus, correlations are cut off at a higher level.

The factor $h(N_A, N_B)$ is calculated by demanding that Eq. (5.16) remain valid in the case where A and B form a *random mixture* at the same composition:

$$g(N_A, N_B, N^*_{AB}) = \frac{(N_A + N_B)!}{N_A!\, N_B!} = h(N_A, N_B)\, \frac{\left[\frac{1}{2} z\,(N_A + N_B)\right]!}{N^*_{AA}!\, N^*_{BB}!\, \left[\left(\frac{N^*_{AB}}{2}\right)!\right]^2} \tag{5.17}$$

where $N^*_{AA} = \dfrac{z}{2}\dfrac{N_A^2}{N_A + N_B}$, $N^*_{BB} = \dfrac{z}{2}\dfrac{N_B^2}{N_A + N_B}$, $N^*_{AB} = \dfrac{z\, N_A\, N_B}{N_A + N_B}$

From Eqs. (5.16) and (5.17) we obtain

$$g(N_A, N_B, N_{AB}) = \frac{(N_A + N_B)!}{N_A!\, N_B!}\, \frac{(N^*_{AA})!\,(N^*_{BB})!\, \left[\left(\frac{1}{2} N^*_{AB}\right)!\right]^2}{\left(\frac{z}{2} N_A - \frac{N_{AB}}{2}\right)!\, \left(\frac{z}{2} N_B - \frac{N_{AB}}{2}\right)!\, \left[\left(\frac{1}{2} N_{AB}\right)!\right]^2} \tag{5.18}$$

We have expressed $g(N_A, N_B, N_{AB})$ in terms of constants and N_{AB} only. The search for the value $\langle N_{AB} \rangle$ that maximizes the term

$$g(N_A, N_B, N_{AB})\; exp\left[-\beta\left(E_A + E_B + \frac{N_{AB}}{z}\, w\right)\right]$$

and for the associated values $\langle N_{AA} \rangle$, $\langle N_{BB} \rangle$, obtainable from $\langle N_{AB} \rangle$ through the counting relations (5.3), leads to the interesting result

$$\frac{\left(\frac{1}{2}\,\langle N_{AB} \rangle\right)^2}{\langle N_{AA} \rangle\, \langle N_{BB} \rangle} = exp\left(-2\beta \frac{w}{z}\right) \tag{5.19}$$

Eq. (5.19) can be viewed as a condition for "chemical equilibrium" for the "reaction"

$$AA + BB \rightarrow AB + BA$$

with associated "standard Gibbs energy of reaction"

$$\Delta G^0 = N_{Avo}\,(2\, w_{AB} - w_{AA} - w_{BB}) = \frac{2}{z}\, w\, N_{Avo}$$

The origin of the name *quasichemical approximation* lies in this observation.

Deriving the mixture thermodynamics from Eq. (5.19) by invoking the maximum term approximation is straightforward, albeit somewhat cumbersome. An expression for the excess Helmholtz energy, from which the activity coefficients can be deduced, is given in [Prausnitz 1986].

In Fig. 5.4, the binodal curve predicted by the quasichemical approximation is shown along with the exact and Bragg-Williams results. It is seen that the inclusion of two-molecule correlations in the quasichemical theory improves the quality of predictions substantially. Nevertheless, the approximation, as any mean field approximation, is bound to fail in the immediate vicinity of the critical point.

5.3 Derivation of the van der Waals Equation of State

The equation of state of Johannes Diderik van der Waals (Ph.D. Thesis Leiden, Holland, 1873; Nobel Prize 1910) was an intellectual landmark. Although based on a quantitatively inexact mean field treatment, the equation accomplished a unified explanation of all experimental knowledge of fluid behavior at the time of its development. It accounted for deviations from the ideal gas law, predicted gas-liquid equilibrium and the existence of critical points, and provided support to the molecular hypothesis. Here we present a simple derivation of the van der Waals equation, pointing out the mean field approximations on which it relies.

As starting point for the derivation of the equation of state we use the exact equations (4.39) and (4.38), which relate pressure to the volume-dependence of the configu-

rational integral in the canonical ensemble. Furthermore, we will introduce a pairwise additivity approximation for the potential energy function:

$$\mathcal{V}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \sum_{i=1}^{N} \sum_{j=i+1}^{N} \mathcal{V}_{pair}(|\mathbf{r}_i - \mathbf{r}_j|) \equiv \sum_{i} \sum_{j>i} \mathcal{V}_{pair}(r_{ij}) \tag{5.20}$$

Van der Waals' formulation rests upon some insightful realizations about the pair potential function $\mathcal{V}_{pair}(r_{ij})$. In a typical fluid, $\mathcal{V}_{pair}$ consists of a harshly repulsive and a smooth attractive part. Furthermore, the structure of the fluid is governed mainly by the harsh repulsive forces and is relatively insensitive to the weak attractive "tail", which dies out rapidly with increasing intermolecular distance. In our subsequent analysis we will assume the following form for the pair potential (see Figure 5.5 *(a)*):

$$\mathcal{V}_{pair}(r) = \begin{cases} \mathcal{V}_{pair}^{rep}(r) = \infty, & \text{if } r \leq \sigma \ ; \\ \mathcal{V}_{pair}^{att}(r), & \text{if } r > \sigma \end{cases} \tag{5.21}$$

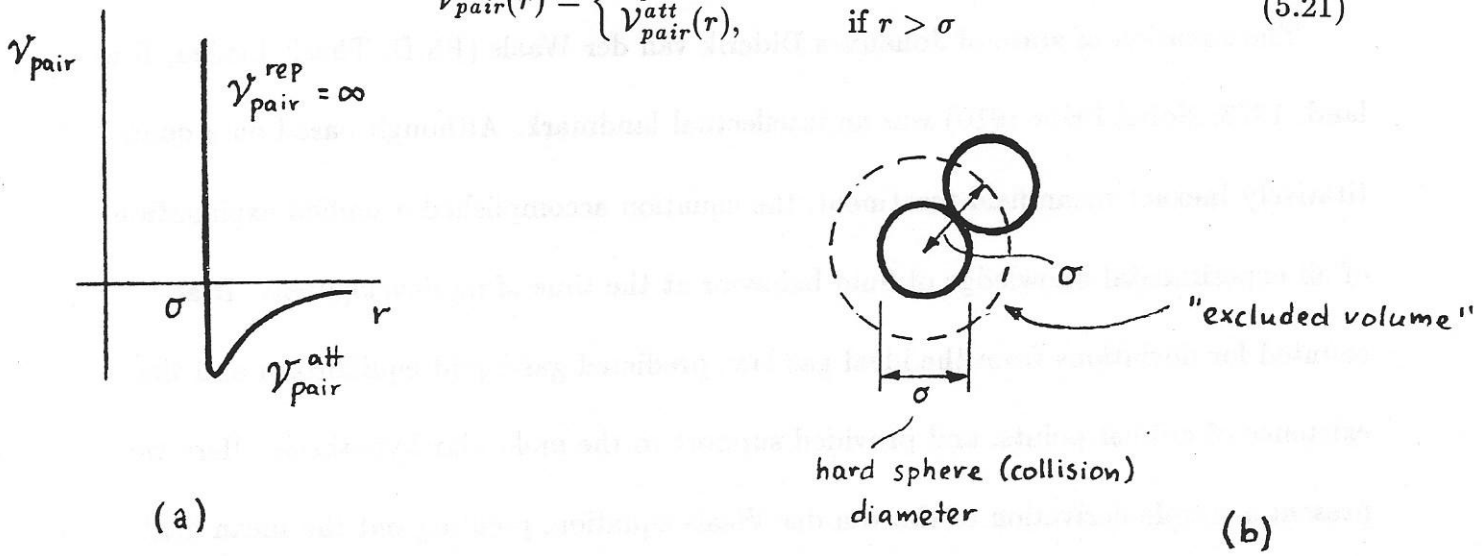

Figure 5.5 *(a)* Approximate shape of the pair interaction potential in a fluid. *(b)* Definition of the hard sphere diameter and of the excluded volume of a molecule.

When the distance between the centers of two molecules becomes smaller than the "hard sphere" (or "collision") diameter σ, the pair interaction is infinitely repulsive.

Consequently, a sphere of radius σ centered at the center of a molecule can never be penetrated by the centers of other molecules. The volume of that sphere is called *excluded volume* of the molecule (Figure 5.5*(b)*).

With the potential energy function of Eq. (5.21), the configurational integral, Eq. (4.38), becomes:

$$Z(N,V,T) = \int \exp\left[-\beta \mathcal{V}^{rep}(\mathbf{r}_1,\ldots,\mathbf{r}_N)\right] \; exp\left[-\beta \mathcal{V}^{att}(\mathbf{r}_1,\ldots,\mathbf{r}_N)\right] \; d^3r_1 \ldots d^3r_N \quad (5.22)$$

where $\mathcal{V}^{rep} = \sum_{i} \sum_{j} \mathcal{V}^{rep}_{pair}(r_{ij})$, $\mathcal{V}^{att} = \sum_{i} \sum_{j} \mathcal{V}^{att}_{pair}(r_{ij})$.

Mean field treatment of attractive interactions The attractive potential energy function appearing in Eq. (5.22) can be written as a sum of contributions from individual molecules:

$$\mathcal{V}^{att}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) = \frac{1}{2}\sum_{i=1}^{N}\left(\sum_{\substack{j=1\\ j\neq i}}^{N} \mathcal{V}^{att}_{pair}(r_{ij})\right)$$

$$\equiv \frac{1}{2}\sum_{i=1}^{N} \mathcal{V}^{att}_{i}(\mathbf{r}_i;\, \mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_{i-1},\mathbf{r}_{i+1},\ldots,\mathbf{r}_N)$$

The above expression is exact within the framework of pairwise additivity. The prefactor $\frac{1}{2}$ ensures that interactions are not doublecounted. The attractive potential energy $\mathcal{V}^{att}_i$ "felt" by a given molecule i due to all other molecules in the system is a function of configuration. We now choose to *neglect* its configuration dependence, and substitute it by a *mean attractive field* $\mathcal{V}^{att}_{MF,i}$:

$$\mathcal{V}^{att}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) \simeq \mathcal{V}^{att}_{MF} = \frac{1}{2}\sum_{i=1}^{N} \mathcal{V}^{att}_{MF,i} \quad (5.23)$$

For the estimation of $\mathcal{V}^{att}_{MF,i}$ we consider the centers of all molecules outside the excluded volume of molecule i as constituting a "smeared" background of uniform density $\rho = N/V$, equal to the overall molecular density of the system. (see Figure 5.6*(a)*) The "smeared" backround extends over radial distances $\sigma \leq r < \infty$ from the center of molecule i. Note that this mean field treatment of attractive interactions *ignores any two-body correlations at distances* $r \geq \sigma$. (In the terminology of the following chapters, it amounts to approximating the pair distribution function of the fluid by a step function at $r = \sigma$). $\mathcal{V}^{att}_{MF,i}$ can thus be written as

$$\mathcal{V}^{att}_{MF,i} = \int_{\sigma}^{\infty} 4\pi\, r^2\, dr\, \rho\, \mathcal{V}^{att}_{pair}(r) \tag{5.24}$$

Note that $4\pi\, r^2\, dr\, \rho$ is the number of molecules within a spherical shell of the smeared background of Fig. 5.6*(a)* centered at the center of i with inner radius r and outer radius $r + dr$. Inasmuch $\mathcal{V}^{att}_{MF,i}$, and therefore $\mathcal{V}^{att}_{MF}$ [Eq. (5.23)] are independent of the system configuration, the Boltzmann factor of the attractive energy can be factored out of the configurational integral of Eq. (5.22), leading to

$$Z(N,V,T) = exp\left[-\beta\frac{N}{2}\int_{\sigma}^{\infty} 4\pi\, r^2\, dr\, \rho\, \mathcal{V}^{att}_{pair}(r)\right] \times$$

$$\int exp\left[-\beta\mathcal{V}^{rep}(\mathbf{r}_1,\ldots,\mathbf{r}_N)\right]\, d^3r_1 \ldots d^3r_N \tag{5.25}$$

or

$$Z(N,V,T) = Z^{att}(N,V,T)\; Z^{rep}(N,V) \tag{5.26}$$

where

$$Z^{att}(N,V,T) = exp\left[-\beta\frac{N^2}{V}\,2\pi\int_{\sigma}^{\infty}\mathcal{V}^{att}_{pair}(r)\, r^2\, dr\right] \tag{5.27}$$

$$Z^{rep}(N,V) = \int exp[\mathcal{V}^{rep}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)]\, d^3r_1 \ldots d^3r_N = \int_{\text{no overlap}} d^3r_1\, d^3r_2 \ldots d^3r_N \tag{5.28}$$

The last expression for $Z^{rep}(N,V)$ in Eq. (5.28) stems from the realization that the Boltzmann factor of the repulsive potential energy is either 0 (for configurations where at least two of the molecular hard sphere cores of diameter σ overlap) or 1 (for configurations where no overlap occurs). The integral in that expression is taken over all nonoverlapping configurations of N hard spheres in volume V. Because of the hard-sphere nature of the repulsive potential, Z^{rep} is independent of temperature.

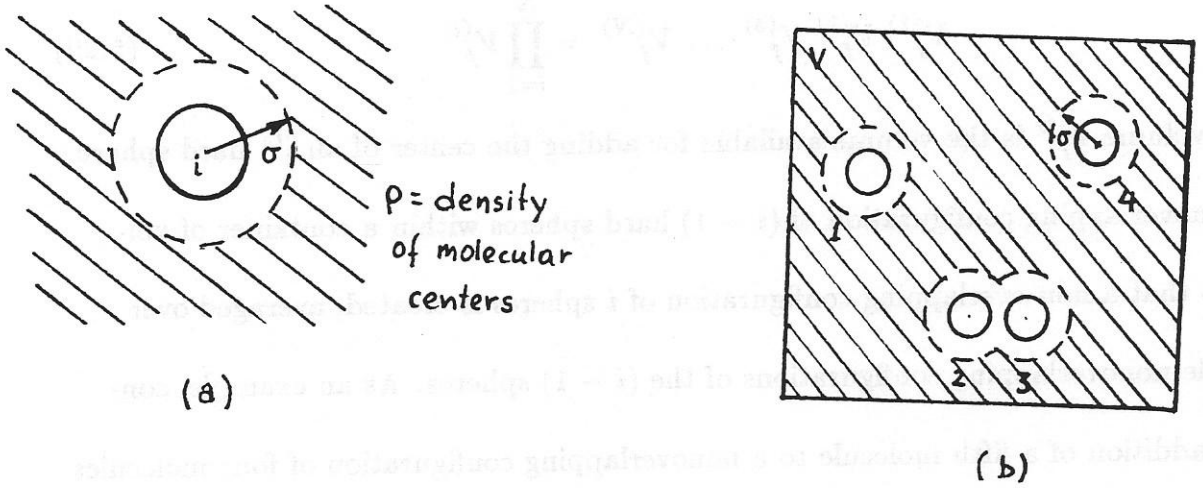

Figure 5.6 *(a)* Smearing of molecular centers around a given molecule invoked in mean field approximation to the attractive interaction energy; *(b)* Illustration of the free volume available for addition of a fifth molecule to a configuration of four nonoverlapping molecules.

Approximate Calculation of $Z^{rep}(N,V)$ The repulsive configurational integral of Eq. (5.28) is not easy to calculate analytically (in fact, its calculation amounts to deter-

mining the thermodynamics of the hard sphere fluid in three dimensions, a problem for which no exact analytical solution but some good approximations exist). In the van der Waals approach, this integral is written as a product of "free volumes" available for addition of the 1^{st}, 2^{nd}, ..., N^{th} particle:

$$Z^{rep}(N,V) = \int d^3r_1 \, \frac{\int_{\text{no overlap}} d^3r_1 \, d^3r_2}{\int d^3r_1} \, \frac{\int_{\text{no overlap}} d^3r_1 \, d^3r_2 \, d^3r_3}{\int_{\text{no overlap}} d^3r_1 \, d^3r_2} \cdots \times$$

$$\frac{\int_{\text{no overlap}} d^3r_1 \, d^3r_2 \, \ldots \, d^3r_N}{\int_{\text{no overlap}} d^3r_1 \, d^3r_2 \, d^3r_{N-1}} \equiv$$

$$V_f^{(1)} \, V_f^{(2)} \, V_f^{(3)} \, \ldots \, V_f^{(N)} = \prod_{i=1}^{N} V_f^{(i)} \tag{5.29}$$

The free volume $V_f^{(i)}$ is the volume available for adding the center of an i^{th} hard sphere into a nonoverlapping configuration of $(i-1)$ hard spheres within a container of volume V so that a non-overlapping configuration of i spheres is created, averaged over all possible nonoverlapping configurations of the $(i-1)$ spheres. As an example, consider the addition of a fifth molecule to a nonoverlapping configuration of four molecules (Fig. 5.6*(b)*). The crosshatched region, lying outside the excluded volumes of the four molecules, is the volume in which the center of the fifth molecule can go. The quantity $V_f^{(5)}$ is the result of averaging the crosshatched volume over all nonoverlapping configurations of the four molecules.

The excluded volume of one molecule [compare Fig. 5.5*(b)*] is

$$v_e = \frac{4}{3} \pi \sigma^3 \tag{5.30}$$

Clearly,

$$V_f^{(1)} = V$$

$$V_f^{(2)} = V - v_e$$

van der Waals approximation for the free volume We now postulate that

$$V_f^{(i)} = V - (i-1)\,v_e \quad \text{for all } i \tag{5.31}$$

Eq. (5.31) is exact for $i = 1$ and $i = 2$, but not for higher values of i. It underestimates $V_f^{(i)}$, as it fails to recognize that the excluded volume spheres of molecules $1, 2, \ldots, i-1$ may actually overlap, hence the total excluded volume may be smaller than the sum of the individual excluded volumes (compare overlap of excluded volumes of molecules 2 and 3 in the lower part of Fig. 5.6*(b)*). Note that the approximation (5.31) ignores three-body and higher correlations among molecules, and is thus a mean-field approximation. All that is accounted for is two-body exclusion. Eq. (5.31) becomes a satisfactory approximation at *low densities*, *i.e.*, under the condition

$$N\,v_e << V, \quad \text{or} \quad \rho\,v_e << 1 \tag{5.32}$$

In our analysis we will assume that condition (5.32) is fulfilled. Combining Eq. (5.29) with the approximation (5.31), we obtain

$$Z^{rep}(N,V) = \prod_{i=1}^{N} [V - (i-1)\,v_e] = V^N \prod_{i=1}^{N} \left[1 - (i-1)\,\frac{v_e}{V}\right], \text{ or}$$

$$\frac{Z^{rep}(N,V)}{V^N} = \left[1 - \frac{v_e}{V}\right] \left[1 - 2\,\frac{v_e}{V}\right] \ldots \left[1 - (N-1)\,\frac{v_e}{V}\right] \tag{5.33}$$

In view of the condition, Eq. (5.32), we expand the product of Eq. (5.33), retaining only the first-order term in $\frac{v_e}{V}$:

$$\frac{Z^{rep}(N,V)}{V^N} \simeq 1 - \left[\frac{v_e}{V} + 2\,\frac{v_e}{V} + \cdots + (N-1)\,\frac{v_e}{V}\right] = 1 - \frac{v_e}{V}\,[1 + 2 + \cdots + (N-1)] =$$

$$1 - \frac{v_e}{V}\,\frac{(N-1)\,N}{2} \simeq 1 - \frac{v_e}{V}\,\frac{N^2}{2} = 1 - \frac{N\,v_e}{2\,V}\,N \simeq \left(1 - \frac{N\,v_e}{2\,V}\right)^N \tag{5.34}$$

where the last substitution is again justified by Eq. (5.32).

Our result for the Z^{rep} term can thus be written

$$Z^{rep}(N,V) = V^N \left(1 - \frac{N\,v_e}{2\,V}\right)^N = V^N \left(1 - \frac{N}{V}\,\frac{2}{3}\,\pi\,\sigma^3\right)^N \tag{5.35}$$

It is convenient to introduce the notation

$$a = -2\pi\,N_{Avo}^2 \int_{\sigma}^{\infty} \mathcal{V}_{pair}^{att}(r)\,r^2\,dr \tag{5.36}$$

$$b = N_{Avo}\,\frac{2}{3}\pi\,\sigma^3 = N_{Avo}\,4\,v_{HS} = N_{Avo}\,\frac{v_e}{2} \tag{5.37}$$

where $v_{HS} = v_e/8$ is the molecular hard-sphere volume.

Eqs. (5.26), (5.27), (5.35)-(5.37) give

$$Z(N,V,T) = exp\left(\beta\,a\,\frac{N^2}{V\,N_{Avo}^2}\right)\; V^N \left(1 - \frac{N\,b}{V\,N_{Avo}}\right)^N \quad \text{or}$$

$$\ln Z(N,V,T) = N\,\ln V + N\,\ln\left(1 - \frac{N\,b}{V\,N_{Avo}}\right) + \frac{1}{k_B\,T}\,a\,\frac{N^2}{V\,N_{Avo}^2} \tag{5.38}$$

Invoking Eq. (4.39),

$$P = k_B\,T\left(\frac{\partial \ln Z}{\partial V}\right)_{T,N} = k_B\,T\left[\frac{N}{V} + \frac{N^2\,b}{V^2\,N_{Avo}}\,\frac{1}{1 - \frac{N\,b}{V\,N_{Avo}}} - \frac{1}{k_B\,T}\,a\,\frac{N^2}{V^2\,N_{Avo}^2}\right] \tag{5.39}$$

Realizing that $\frac{V N_{Avo}}{N} = v$, the molar volume of the fluid, we obtain from Eq. (5.39)

$$P = RT\left[\frac{1}{v} + \frac{b}{v^2}\frac{1}{1-\frac{b}{v}}\right] - \frac{a}{v^2} = \frac{RT}{v}\frac{1}{1-\frac{b}{v}} - \frac{a}{v^2} = \frac{RT}{v-b} - \frac{a}{v^2}, \text{ or}$$

$$\left(P + \frac{a}{v^2}\right)(v-b) = RT \tag{5.40}$$

which is the familiar van der Waals equation of state.

The hard-sphere equation of state obtained from the van der Waals by setting $a = 0$ is exact in one dimension (Tonks gas), but inaccurate in three dimensions. Much more accurate equations of state (*e.g.*, Carnahan-Starling) exist today for the three-dimensional hard-sphere fluid. The concept of short-range repulsive and long-range attractive forces among molecules and the idea that fluid structure is dictated by the former have played a very important role in modern liquid theory. In a sense, van der Waals introduced the first perturbation theory, relying upon the hard-sphere fluid as a reference fluid.

References

Lambert, S.M., Soane, D.S., and Prausnitz, J.M. (1992). Liquid-liquid equilibria in binary systems: Monte Carlo simulations for calculating the effect of nonrandom mixing. Presented at the Sixth International Conference on Fluid Properties and Phase Equilibria for Chemical Process Design, July 19-24, 1992. Cortina d' Ampezzo, Italy. Fluid Phase Equilibria (1993) 83, 59-68.

Lifshitz, E.M., Pitaevskii, L.P. (1980). *Statistical Physics* (Vol.5 of Landau and Lifshitz Course of Theoretical Physics), 3rd Ed., Part 1. Pergamon Press, Oxford.

Lupis C.H.P. (1983). *Chemical Thermodynamics of Materials.* Elsevier, Amsterdam

Prausnitz J.M., Lichtenthaler R.N., Azevedo E.G. (1986) *Molecular Thermodynamics of Fluid Phase Equilibria.* 2nd Ed., Prentice-Hall, Englewood Cliffs.

Scesney P.E. (1970) Mobile-Electron Ising Ferromagnet. Phys. Rev. B **1**(5), 2274-2288.

Wilson, K.G.; Kogut, J. (1974). The renormalization group and the ϵ expansion *Phys. Rep.* **12**, 75-200.