Entropic Phase Separation

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The Heavens declare the glory of God;
the skies proclaim the work of his hands.

Day after day they pour forth speech;
night after night they display knowledge.

There is no speech or language
where their voice is not heard.

Psalm 19:1-3

Abstract

Any elementary textbook on statistical mechanics will try to convince you that energy is everything w.r.t. phase separation. The goal of this thesis is to show otherwise.

Contents

Introduction

Entropic ordering is an ubiquitus phenomenon. Due to it's counter-intuitive nature, it is not widely appreciated in the Physics Community as a whole. This thesis will concentrate on one type of entropic ordering transition, namely entropic phase separation.

- Chapter 1 will concentrate on basic liquid theory as can be found in the standard book by J-P. Hansen and I.R. McDonald[1]. This has been done to set notation, and to make a connection with later chapters.

- In chapter 2 some of the liquid theory will be generalized to the case of binary hard-sphere mixtures, with a special emphasis on the possibibility of phase-separation. The work of Thierry Biben and Jean-Pierre Hansen reopened this question recently [21, 22, 23, 30].

- The fourth chapter will concentrate on the lattice models developped by Daan Frenkel and myself [45] to try to understand some aspects of the work of Biben and Hansen.

- A Chapter (4) has also been added on general characteristics of entropic phase transitions. It's aimed at that part of the Physics community that does not concentrate on aspects of Statistical Mechanics. For this reason, it is more or less self-contained, with references mainly to figures in the rest of the text[1] , and has a pedagogical character.

- Of course the last chapter contains conclusions and a lengthy discussion of various aspects of solvent-induced entropic attraction.

The Bibliography also includes some notes on many-fermion simulations which I hope to write up in full soon.

[1] it only has one (well known) formula!

Chapter 1

Some Basics of Equilibrium Liquid Theory [1]

1.1 Formal Manipulations

The equilibrium statistical properties of a many-particle system are contained in what is called the *partition function*, which is simply the (weighed) sum of states accessible to the system. Statistical Mechanics concerns itself either with the direct calculation of such a function, or with deducing properties of a system from it. In general, the calculation of the partition function for macroscopic systems is prohibitively difficult. Fortunately, it does not have to be explicitly calculated to obtain many of the (approximate) properties of a system.

This chapter will concern itself with deriving properties and relations between properties of many particle systems when the full partition function is not known. The reader will have to wait till chapter 3 to encounter one of the rare situations where the it can be calculated explicitly.

A system with the chemical potential μ, volume V and temperature T fixed, is described by the so-called *grand canonical partition function*. For a system consisting of classical, identical particles, interacting with a pair-wise additive potential $v(i,j)$ and in some spatially dependent external field $\phi(i)$, the sum of states accessible to the system, weighed such as to obtain the grand canonical partition function is:

$$\Xi = \sum_{N=0}^{\infty} \frac{1}{N!} \int \dots \int \prod_{i=1}^{N} z^*(i) \prod_{i<j}^{N} e(i,j) d1 \dots dN \tag{1.1}$$

[1] This chapter leans heavily on [1] and more or less reproduces what can be read there. The rest of this report uses their notation as well. The reader familiar with the first 5 chapters of [1] can skip this chapter.

where : $z^*(i) = zexp(-\beta\phi(i))$, and $e(i,j) = exp(-\beta v(i,j))$
Here z is the activity, β is the inverse temperature times boltzmann's constant and i and j denote the spatial coordinates of particle i and j respectively (the momentum coordinates have been integrated out and can be included in the definition of the fugacity).

Now consider the effect of the variation of z^* on Ξ:

$$\delta\Xi = \sum_{N=0}^{\infty} \frac{1}{N!} \sum_{k=1}^{N} \int \dots \int \prod_{i \neq k} z^*(i) \delta z^*(k) \prod_{i<j} e(i,j) d1 \dots dN \tag{1.2}$$

All particles are identical so that together with the standard theory of functional differentiation this gives:

$$\frac{\delta\Xi}{\delta z^*(1)} = \frac{1}{z^*(1)} \sum_{N=1}^{\infty} \frac{1}{(N-1)!} \int \dots \int \prod_{i=1}^{N} z^*(i) \prod_{i<j}^{N} e(i,j) d2 \dots dN \tag{1.3}$$

The n-particle distribution function $\rho^{(n)}$ is defined as $N!/(N-n)!$ times the probability to find n particles of the system in the volume element $d\mathbf{r}^n$ irrespective of all N momentum coordinates as well as the $(N-n)$ spatial coordinates of all other particles. It follows that the one-particle distribution function is the partition function with one set of spatial coordinates not integrated out divided by the full function. In terms of the functional derivatives this means:

$$\rho^{(1)}(1) = \frac{\delta \log \Xi}{\delta \log z^*(1)} \tag{1.4}$$

A generalization gives:

$$\rho^{(n)}(1, \dots, n) = \frac{1}{\Xi} z^*(1) \dots z^*(n) \frac{\delta^n \log \Xi}{\delta z^*(1) \dots \delta z^*(n)} \tag{1.5}$$

Writing out the sum of (1.1) and expressing each term diagramatically gives:

$\Xi =$ $1+$ [all diagrams consisting of black z^* circles with an e-bond linking each pair of circles]

$$\Xi = 1+ \tag{1.6}$$

where each diagram represents an integral in the sum over N. Higher order terms still contribute strongly to the series and are of order V^N because $e(i,j) \rightarrow 1$

when the interparticle distance exceeds the range of the potential However, one can introduce the related function

$$f(i,j) = e(i,j) - 1 \tag{1.7}$$

which clearly goes to zero. If this is substituted into (1.6) the expansion becomes:

$\Xi =$ 1+ [all diagrams consisting of black z^* circles and at most one f-bond linking each pair of circles]

$$\Xi = 1+ \tag{1.8}$$

Higher order terms don't go as V^N anymore, but this has been achieved at the expence of adding many more diagrams. Powerful graph-theoretical tools like the lemma which states that the exponent of so called "topologically distinct star-irreducible" diagrams = 1 + the set of all such diagrams and their so called star products [1] [2], together with identities like (1.5) derived by functional differentiation can be used to tackle this expansion. One very useful expansion that can be derived in this way (see [1] for details and definitions) is:

$\log[\frac{\rho^{(1)}(\vec{\mathbf{r}})}{z^*(\vec{\mathbf{r}})}] =$ 1+ [all simple, irreducible diagrams[3]consisting of one white 1 circle labelled $\vec{\mathbf{r}}$, one or more black $\rho^{(1)}$ circles and f-bonds]

$$\log[\frac{\rho^{(1)}(\vec{\mathbf{r}})}{z^*(\vec{\mathbf{r}})}] = 1+ \tag{1.9}$$

If the density $\rho^{(1)}(\vec{\mathbf{r}})$ is the same everywhere, then the diagrams reduce to the ρ^i times the well known Mayer cluster integrals, which can be derived in different ways (see for eg. [3]).

Using (1.5) one can show that:

$$\frac{\delta\rho^{(1)}(1)}{\delta\log(z^*(2)}=z^*(2)\frac{\delta z^*(1)}{\delta z^*(2)}\frac{\delta\log\Xi}{\delta z^*(1)}+z^*(2)z^*(1)\frac{\delta^2\log\Xi}{\delta z^*(1)\delta z^*(2)} \tag{1.10}$$

[2]A similar lemma is used in the context quantum many particle theory when deriving Feynman rules for expansions of Green's functions. ([2] p 96)

[3]Simple means no pair of circles is connected by more than one f bond, and irreducible means that the diagram can't be split into more components of which at least one contains no white circle.

This can be rewritten using the relation :

$$\delta(1,2) = \frac{\delta z^*(1)}{\delta z^*(2)} \tag{1.11}$$

for the first term together with the following definition of the *pair correlation function* [1]:

$$h(1,2) = \frac{\rho^{(2)}(1,2) - \rho^{(1)}(1)\rho^{(1)}(2)}{\rho^{(1)}(1)\rho^{(1)}(2)} \tag{1.12}$$

for the second term to obtain the relation:

$$\frac{\delta\rho^{(1)}(1)}{\delta\log(z^*(2))} = \rho^{(1)}(1)\delta(1,2) + \rho^{(1)}(1)\rho^{(1)}(2)h(1,2) \tag{1.13}$$

One can also define the *direct correlation function* [1] as:

$$\begin{aligned} c(1,2) &= \frac{\delta\log[\rho^{(1)}(1)/z^*(1)]}{\delta\rho^{(1)}(2)} \\ &= \frac{\delta(1,2)}{\rho^{(1)}(1)} - \frac{\delta\log z*(1)}{\delta\rho^{(1)}(2)} \end{aligned} \tag{1.14}$$

Together with (1.9) and the fact that the functional differentiation will make one of the black circles white (= fixed instead of integrated out) it is clear that the diagrammatic expansion for c(1,2) becomes:

$c(1,2) =$ [all simple, diagrams that consist of two white 1-circles labelled 1 and 2, black $\rho^{(1)}(1)$circles and f-bonds, and are free of connecting circles [4].]

$c(1,2) =$

(1.15)

The diagrams of (1.9) are irreducible, and as they contain only one white circle this is equivalent to not having any connecting circles as well, which still holds if you whiten a black circle of course. A relation between the direct correlation function (1.14) and the pair correlation function (1.12) can be obtained by inserting (1.14) and (1.13) into the following representation of the δ function:

$$\delta(1,2) = \int \frac{\delta\log z^*(1)}{\delta\rho^{(1)}(3)} \frac{\delta\rho^{(1)}(3)}{\delta\log z^*(2)} d3 \tag{1.16}$$

[4] If you erase a connecting circle, the diagram splits into two components.

to obtain:

$$h(1,2) = c(1,2) + \int \rho^{(1)}(3)c(1,3)h(3,2)d3 \tag{1.17}$$

which is the well known *Ornstein Zernike (OZ)* relation.

By solving (1.17) recursively one obtains a series expantion of $h(1,2)$ in powers of $c(1,2)$. This can most easily be pictured diagramatically as:

$$h(1,2) = \qquad\qquad ; \tag{1.18}$$

The bonds are c functions and the black dots denote $\rho^{(1)}(1)$'s and the white circles are simply the two terminal points. The diagrams show where the direct correlation function gets it's name, as $h(1,2)$ is the sum of a direct correlation between particles 1 and 2, together with correlations which pass indirectly between an increasing number of other particles [5]. By simply filling in the diagrams for $c(1,2)$ (1.15), into (1.18) one obtains a diagrammatic expansion for $h(1,2)$. Adding the diagram pairs together which are the same except for an f-bond between the two white circles, and using the definition (1.7) for the f-bonds gives a density expansion for the so called *radial distribution function*:

$$\begin{aligned} g(1,2) &= h(1,2) + 1 \\ g(1,2) &= \text{[all simple diagrams consisting of two white 1 circles labelled} \\ &\quad \text{1 and 2, linked by an e-bond, black } \rho^{(1)}(1) \text{ circles and} \\ &\quad \text{f-bonds, and are free of connecting circles]} \end{aligned} \tag{1.19}$$

Because the e-bond can be written as $exp[-\beta v(1,2)]$, the diagrams are usually written as :

$$g(1,2) = exp[-\beta v(1,2)] \left(1 + \sum_{n=1}^{\infty} \rho^n g_n(1,2) \right) \tag{1.20}$$

where the $g_n(1,2)$ represent the n^{th} order diagrams.(see table (1.1))

After all this one may wonder why all the different kinds of functions and diagrams? The diagrams are far to numerous to calculate, and the higher order one's can't even be calculated. It isn't clear why two kinds of correlation functions need to be defined either if you can't calculate them.

[5] The attentive reader may have noticed that one could also obtain a similar expansion for $c(1,2)$ in terms of $h(1,2)$. This is true, but the series would be an alternating one so that an interpretation as a sum of correlations breaks down

Table 1.1: Graphical representation of the graphs retained in various approximations of the g_n (taken from [4])

To answer this, note to begin that the two types of correlation functions have different properties. While h(1,2) (and the related g(1,2)) is directly experimentally accessible and can be related to many physical properties, it is in general quite long ranged. On the other hand, c(1,2) is generally quite short ranged as can be seen from the limit $\| 1-2 \| \to \infty$. In first order c(1,2) is equal to $f(1,2)$, and higher order terms go at least as $f(1,2)^2$ so that it tends to zero linearly in the potential, and has roughly the same range as well. Some of the most succesfull approximative schemes consist of utilizing the different properties of the two kinds of correlation functions to obtain some relation between h(1,2) and c(1,2), which in turn gives a closure of the OZ relation (1.17). These closures then correspond to approximating g(1,2) by summing and infinite subclass of diagrams.

1.2 Approximative methods

The remainder of this chapter will concern itself with two such approximations, and a mixture of the two. They were originally derived from diagrammatic considerations, but they can be derived much more elegantly using functional talyor expansions [6]. The arguments that follow were first put forth by J.K. Percus (see [1] for references).

Consider a system of identical particles, and place an extra particle at the origin. The interaction it feels with other particles is then interpreted as an external field $\Delta\Phi(i) = v(0,1)$ Percus then shows that for a homogeneous system:

$$\rho^{(1)}(i \mid \phi) = \rho g(0,i) \tag{1.21}$$

The change in density when the potential is changed from ϕ to $\phi + \Delta\phi$ is:

$$\Delta\rho^{(1)}(i) = \rho h(0,i) \tag{1.22}$$

Functional talyor expansions in $\Delta\phi$ or in the response $\Delta\rho$, both of which can be seen as perturbations in a large system, give the desired relations between h(1,2) and c(1,2). If one expands $\rho^{(1)}(i \mid \phi)/z^*(1)$ in powers of the response then :

$$\begin{aligned}
\frac{\rho^{(1)}(1 \mid \phi)}{z^*(1)} &= \frac{\rho^{(1)}(1 \mid 0)}{z} \\
&+ \int \left(\frac{\delta}{\delta\rho^{(1)}(2 \mid \phi)} \frac{\rho^{(1)}(1 \mid \phi)}{z^*(1)} \right)_{\phi=0} [\rho^{(1)}(2 \mid \phi) - \rho^{(1)}(2 \mid 0)] d2 \\
&= \frac{\rho}{z} + \frac{\rho^2}{z} \int c(1,2) h(2,0) d2 \qquad (1.23)
\end{aligned}$$

[6]This section draws heavily on [1]

where (1.22) and (1.14) were used. Applying (1.22) again gives:

$$exp[-\beta v(0,1)]g(0,1) = 1 + \rho \int c(1,2)h(2,0)d2 \tag{1.24}$$

By substituting into the OZ relationship (1.17) one obtains:

$$c(1,2) = (1 - exp[+\beta v(1,2)])g(1,2) \tag{1.25}$$

which is the kind or relation between the two correlation functions we set out to find. When (1.25) is again substituted into the OZ relation, one obtains a non-linear integral equation for $g(\vec{\mathbf{r}})$ in terms of the potential:

$$exp[\beta v(\vec{\mathbf{r}})]g(\vec{\mathbf{r}}) = 1 + \rho \int [g(\vec{\mathbf{r}} - \vec{\mathbf{r}}\,') - 1][1 - exp[\beta v(\vec{\mathbf{r}}\,')]g(\vec{\mathbf{r}}\,')d\vec{\mathbf{r}}\,' \tag{1.26}$$

This is known as the Percus-Yevick equatin after it's discoverers [5].

Another well known relation between the correlation functions can be obtained by truncating a functional Taylor expansion of $log[\rho^{(1)}(1 \mid \phi)/z^*(1)]$ in $\Delta\rho$. This gives the following relation :

$$c(\vec{\mathbf{r}}) = -\beta v(\vec{\mathbf{r}}) + h(\vec{\mathbf{r}}) - \log[h(\vec{\mathbf{r}}) + 1] \tag{1.27}$$

which together with the OZ relation gives the HNC integral equation:

$$log(g(\vec{\mathbf{r}})) + \beta v(\vec{\mathbf{r}}) = \rho \int [g(\vec{\mathbf{r}} - \vec{\mathbf{r}}\,') - 1][g(\vec{\mathbf{r}}\,') - \log[g(\vec{\mathbf{r}}\,')] - \beta v(\vec{\mathbf{r}}\,')]d\vec{\mathbf{r}}\,' \tag{1.28}$$

which was first derived by a diagramatic method [6].

From table 1 it is clear that the PY approximation omits many more diagrams than HNC [7]. Nevertheless, it turns out that the PY approximation is superior to HNC for short ranged potentials. This stems from a cancellation of errors. HNC does seem to be superior for long-ranged ones [1]. An especially appealing aspect of the PY integral equation is that it can be solved exactly for hard spheres, as was first shown by Wertheim and Thiele independently of each other [11]. The method used by Wertheim is especially elegant [8]. He first rewrites the OZ relation in terms of bipolar coordinates, and Laplace transforms. The functions obtained are then combined so as to make an *entire* function in the complex plane. He then applies a theorem due to Rouché that states that if an entire function behaves like z^n for $z \to \infty$ then it can only be a polynomial of degree n. In this case the combined function turns out to be a second order

[7] A nice exposition of which diagrams are omitted can be found in [7] p. 380

[8] See [4] for a cleaned up version of his arguments. Note that the definition of bipolar coordinates does not correspond to that found in many standard references

polynomial. From this beautiful simplification Wertheim derives the following direct correlation function:

$$
\begin{array}{lcr}
c(\mathbf{r}^*) = & (1-\eta)^{-4}[-(1+2\eta)^2 + 6\eta(1+\frac{1}{2}\eta)^2\mathbf{r}^* - \frac{1}{2}\eta(1+2\eta)^2\mathbf{r}^{*\mathbf{3}} & \mathbf{r}^* < 1 \\
c(\mathbf{r}^*) = & 0 & \mathbf{r}^* > 1
\end{array}
\tag{1.29}
$$

where $\mathbf{r}^*$ is $\mathbf{r}$ divided by the hard-sphere diameter σ, and $\eta = \pi\sigma/6$ is the packing fraction. From the compressibility relation [1] :

$$\rho\hat{c}(0) = 1 - \chi_T^0/\chi_T \tag{1.30}$$

an equation of state can be derived by integrating to give:

$$\frac{\beta p^c}{\rho} = \frac{1+\eta+\eta^2}{(1-\eta)^3} \tag{1.31}$$

The superscript c refers to the fact that this is the compressibility equation of state. By filling in the contact values of the radial distribution function into the virial equation [1]:

$$\frac{\beta p}{\rho} = 1 + \frac{2}{3}\pi\rho\sigma^3 g(\sigma) \tag{1.32}$$

one obtains the so-called virial (^{v}) equation of state:

$$\frac{\beta p^v}{\rho} = \frac{1+2\eta+3\eta^2}{(1-\eta)^2} \tag{1.33}$$

If the PY approximation were exact, (1.31) and (1.33) would be the same. As is stands, the compressibility equation over estimates and the virial equation underestimates the real pressure as a function of the packing fraction η. The HNC equations can only be solved numerically, and the compressibility/virial equations underestimate/overestimate the pressure, just the opposite of the PY equations. Perhaps the underestimate of the HNC virial pressure can be understood in that the neglected diagrams, the so-called bridge functions, are negative [12]. When subtracted from the left side of (1.27) they cause the real $h(\sigma)$ to be underestimated.

The fact that the approximations give two different equations of state (virial and compressibility) has motivated a lot of "thermodynamically consistent" closures. These have some parameter(s) which is (are) varied to enforce consistency between the two types of equations of state. The fact that PY is superior at short distances, and HNC at long distances has been used by F. Rogers and

D. Young [13] to obtain a closure which interpolates between the two approximations with a parameter to enforce thermodynamic consistency. Their closure approximation (RY) is defined as:

$$g(\mathbf{r}) = \Theta(\mathbf{r} - \sigma)\left(1 + \frac{exp[(h(\mathbf{r}) - c(\mathbf{r}))(1 - exp[-\xi\mathbf{r}])] - 1}{1 - exp[-\xi\mathbf{r}]}\right) \tag{1.34}$$

for hard spheres. The Θ function is the usual Heaviside funcition. If $\xi \to 0$ then RY reduces to PY, while if $\xi \to \infty$, it reduces to HNC (for hard spheres). The closure seems to give better results than the other two derived earlier [13].

So at the end of this chapter, an exact, but intractable diagrammatic expansion for $g(\mathbf{r})$ (1.19) has been obtained. Functional differentiation techniques and diagrammatic lemma's have been used to obtain approximate relations between different kinds of correlation functions. These relations can be used to close the OZ (1.17) relation, and can be interpreted as partial summations of infinite subclasses of diagrams, or as the result of a truncated functional taylor expansion. The RY closure (1.34) can be interpreted as a combination of two kinds of summation or expansions. Although these approximations seem to give reasonable quantitative results, it is not always clear why. For example, the PY closure can be obtained by linearizing the HNC closure w.r.t. (h - c). If one were to look at the diagrams, the HNC closure (1.27) retains all the PY closure (1.25) diagrams and many more, and yet it is inferior for hard-sphere's. The formal manipulations have only given limited insight and in that light the more intuitive approach of Shinomoto [14] is quite attractive. By using simple arguments related to depletion interaction [26, 25] (see figure (4.1)), he obtains the following equation of state:

$$\frac{p}{nk_BT} = exp[-\beta(4\eta + 2\eta^2)] \tag{1.35}$$

which is of a different from than the previous equations. Surprisingly it is much more accurate that the two PY equations and almost rivals the Carnahan-Starling equation [20].

Chapter 2

Binary hard-sphere mixtures; Phase Separation?

2.1 Evidence against Phase Separation

Binary mixtures of hard-spheres with dissimilar diameters are perhaps the simplest continuum fluid mixtures imaginable where the only difference between the components is geometric. This makes them interesting as model systems to isolate the effects of size disparity. In practice they even give reasonable predictions for a host of phenomena seen in "real" mixtures. Because of this, they also serve as reference systems for more elaborate theories (see e.g. [1]). In this light the question whether or not such a simple mixture will phase separate is quite important. The discussions of the previous chapter can be generalized and applied to the case of hard-sphere mixtures. Extra attention will be paid to the question of phase-separation.

The Percus-Yevick integral equation was first solved for binary mixtures by J.L. Lebowitz [16] who generalized the arguments of Wertheim [11]. He first defines a generalization of (1.13):

$$\frac{\delta \rho_i^{(1)}(1)}{\delta \log(z_j^*(2))} = \rho_i^{(1)}(1)\delta(1,2)\delta_{ij} + \rho_i^{(1)}(1)\rho_j^{(1)}(2)h_{ij}(1,2) \tag{2.1}$$

where i and j refer to the different components. ($i, j = 1, 2$ in the case of binary mixtures) The same can be done to define generalized direct correlation functions like (1.14):

$$c_{ij}(1,2) = \delta_{ij}\frac{\delta(1,2)}{\rho_i^{(1)}(1)} - \frac{\delta \log z_i^*(1)}{\delta\rho_j^{(1)}(2)} \tag{2.2}$$

By substituting this into a representation of the δ function (1.16), one can obtain the generalized OZ relations:

$$h_{ij}(1,2) = c_{ij}(1,2) + \sum_{l=1,2}\int \rho_l^{(1)}(3)h_{il}(1,3)c_{lj}(3,2)d3 \tag{2.3}$$

Now the OZ relations refer to a set of 4 coupled integral equations of which the two with $i \neq j$ are equal. A generalization of Percus's argument for a one component system, together with a truncated functional Taylor expansion in the response to an extra particle gives the generalized PY equations:

$$c_{ij}(1,2) = (1 - \exp[-\beta v_{ij}(1,2)])\, g_{ij}(1,2) \tag{2.4}$$

Again, there are 3 independent equations. Lebowitz then goes on to solve the coupled PY integral equations:

$$\begin{aligned}\exp[\beta v_{ij}(1,2)]g_{ij}(1,2) = 1 + &\sum_{l=1,2}\int \rho_l^{(1)}(3)(g_{il}(1,3)-1)\\ &(1-\exp[\beta v_{lj}(3,2)])d3\end{aligned} \tag{2.5}$$

Just like Wertheim, he uses to bipolar coordinates and after some manipulations he Laplace transforms. This gives several 2×2 matrices which are rearanged to get matrices with all components being entire functions. He then generalizes Wertheim's elegant arguments together with some more analysis in the complex plane to obtain the direct correlation functions:

$$\begin{aligned}-c_{ii}(\mathbf{r}) &= a_i + b_i\mathbf{r} + d\mathbf{r}^3, & \mathbf{r} < \sigma_i, i = 1,2 &\\ -c_{12}(\mathbf{r}) = -c_{21}(\mathbf{r}) &= & a_1 & \quad \mathbf{r} < \lambda\\ &= & a_1 + [bx^2 + 4\lambda dx^3 + dx^4]/\mathbf{r}, & \quad \lambda \leq \mathbf{r} \leq \sigma_{12}\end{aligned} \tag{2.6}$$

where $\sigma_1(\sigma_2)$ are the diameters of the small (large) spheres, $\lambda = (\sigma_2 - \sigma_1)/2$, $\sigma_{12} = (\sigma_1 + \sigma_2)/2$,$x = \mathbf{r} - \lambda$, and the other (complicated) constants a_i, b_i, b and d can be found in [16] eqn. (38). From the following generalizations of the compressibility equations (1.30)

$$\sum_{i=1,2}\sum_{j=1,2}\rho_i\rho_j\hat{c}_{ij}(k=0) = 1 - \frac{\chi_T^0}{\chi_T} \tag{2.7}$$

and the virial equation (1.32)

$$\beta p^v = \sum_i \rho_i + \frac{2}{3}\pi \sum_{i=1,2}\sum_{j=1,2} \rho_i\rho_j\sigma_{ij}^2 g_{ij}(\sigma_{ij}) \tag{2.8}$$

the compressibility and virial equations of state can be derived:

$$\begin{aligned}\beta p^c &= \left\{ \frac{[\rho_1+\rho_2][1+\xi+\xi^2]}{(1-\xi)^3} \right. \\ &- \left. \frac{(\frac{18}{\pi})(\eta_1\eta_2\sigma_1^{-3}\sigma_2^{-3})(\sigma_1-\sigma_2)^2)[2\sigma_{12}+\sigma_2\eta_1+\eta_2\sigma_1]}{(1-\xi)^3)} \right\} \qquad (2.9) \\ \beta p^v &= \beta p^c - \frac{18}{\pi}\xi(\frac{\sigma_1}{\eta_1}+\frac{\sigma_2}{\eta_2})^3(1-\xi)^{-3} \qquad (2.10)\end{aligned}$$

Here $\eta_i = \frac{1}{6}\pi\rho_i\sigma_i^3$ is the packing fraction [1] and $\xi = \sum_i \eta_i$ is the total packing fraction. For $\sigma_1 = \sigma_2$ this clearly reduces to the one-component equations. From the form of (2.10) it's clear that the compressibility equation gives a higher pressure than the virial one, and just as in the one-component case, simulations [18] show that the real pressure is bounded by the two equations [20] [2]

The thermodynamics of mixtures of hard-sphere's in the PY approximation was first worked out in an infuential paper by Lebowitz and Rowlinson [17], who pay special attention to the possibility of phase-separation. For binary mixtures a sufficient condition for thermodynamic stability is simply that the determinant of the stability matrix $\mathbf{M}$, defined as:

$$M_{ij} = \frac{\delta\mu_i}{\delta\rho_j}, \tag{2.11}$$

is positive definite. In the case of the compressibility equations, they obtain the following manifestly positive definite form:

$$\mid \mathbf{M} \mid = \frac{(1+2\xi)^2}{\beta\rho_1\rho_2(1-\xi)^4} > 0. \tag{2.12}$$

so that the compressibility equations don't give a phase transition, just as is the case for the one-component system. (see also [27] for a similar expression for an n-component mixture) Unfortunately, the stability criterium for the virial equations doesn't reduce to a simple form except for $(\sigma_1/\sigma_2) = 0$, and so Lebowitz

[1] This definition is slightly different from that of [16, 17]

[2] in fact, one of the best semi-emperical equations of state is the Mansoori equation [19] in which one writes $\beta p = \frac{2}{3}\beta p^c + \frac{1}{3}\beta p^v$. For the one-component fluid, the same linear combination is equivalent to the popular and very accurate Carnahan-Starling equation.

and Rowlinson must recourse to numerical calculations. They do this for a variety of packing and mole fractions and for diameter ratio's of $\frac{1}{3}$ up to $\frac{9}{10}$ and find that the determinant is always positive[3].[4]

The thermodynamics of a mixture are often conveniently expressed in terms of the "excess" properties defined as the difference between the mixture and an ideal mixture. If the (Gibbs) free energy of mixing shows a local maximum or even an inflection point as a function of concentration of one of the components, phase separation will occur. To achieve this, a necessary, but not sufficient condition is that the excess Gibbs free energy be positive. (to counteract the negative $x_i \log x_i$ terms). As there is no energy change upon mixing, the excess Gibbs free-energy is given bij:

$$G_E = \int_0^p V^E dp \tag{2.13}$$

where V^E is the excess volume which can be found by numerically solving (2.9) and (2.10). Lebowitz and Rowlinson did this for different values of ξ and σ_1/σ_2, and (almost) always found a negative excess volume. From this they show that (2.13) will always be negative, and so they conclude that there is no phase-separation in a binary mixture, at least not in the PY approximation. Simulations by B.J. Alder [18] seemed to confirm this. At this point it is interesting to note that none of the authors went to more extreme size ratio's than $\frac{1}{3}$. In fact, in [18] this is attributed to the fact that this ratio is already very small when compared to realistic liquid mixtures. Alder states that fluid-fluid phase separation is most likely when the diameter ratio is close to one. There had been some predictions at the time that phase separation would occur then, which explains why special attention was paid to this case.

For many years these results were assumed sufficient proof of a lack of phase-separation in binary hard-sphere mixtures. An example of this can be found on page 124 of [1], one of the standard books of the field, "Perhaps the most interesting result to emerge from this body of work is the fact that, irrespective of the diameter ratio, there is no phase separation in the fluid phase of mixtures of addititve hard spheres.".

2.2 Evidence for Phase Separation

In contrast to earlier authors [18] who were mainly interested in size ratio's pertaining to molecular mixtures, T. Biben and J.P. Hansen [21] applied the binary hard-sphere mixture model to colloidal suspensions and investigated the limit $y = \sigma_1/\sigma_2 \to 0$ where 1 refers to the small solvent and 2 refers to the

[3] I'm trying to check this for more extreme size ratio's. Unfortunately there are some small errors (?)in the Lebowitz Rowlinson expressions.

[4] Jan Dhont has succeeded in checking this for the virial equation of state and has found an instability for size ratio's greater than 1/6 !! I have added his results in an appendix

colloidal particles. n the first of a series of articles [21] found a surprising result within the PY approximation. By separating the length scales in the coupled OZ relations, and taking the limit $y \to 0$, they show that the solvent behaves like a one-component fluid with a density ρ which corresponds to the space left over by the large particles. This is not surprising. However, consider the behavior of $g_{22}(\sigma_2)(see(2.6))$:

$$
\begin{aligned}
-c_{22}(\sigma_2) = g_{22}(\sigma_2) &= \left[1 - \xi + \frac{3}{2}\sigma_2(\frac{\eta_1}{\sigma_1} + \frac{\eta_2}{\sigma_2})\right](1-\xi)^{-2} \\
&= \left[\frac{1-\eta_1+\eta_2/2}{(1-\eta_1-\eta_2)^2} + \frac{3}{2}\frac{\eta_1}{(1-\eta_1-\eta_2)^2}\frac{\mathbf{1}}{\mathbf{y}}\right] \quad (2.14)
\end{aligned}
$$

In the second line the y dependence has been made explicit. If the packing fractions are held constant[5] when taking the limit $y \to 0$, which seems physically reasonable, the second part of (2.14) diverges as $1/y$ while the first part is a kind of "renormalized" $g^*_{22}(\sigma_2)$. In general this can be writen as:

$$
\lim_{y\to 0} g_{22}(\mathbf{r}) = g^*(\mathbf{r}) + C\delta(\mathbf{r} - \sigma_2) \quad (2.15)
$$

where the divergence has been put into the delta function. At finite, but small y, $g_{22}(\mathbf{r})$ has a large peak at contact, and oscillations on the scale of σ_1 near contact. So in contrast to the solvent, the large "solute" spheres do not reduce to a one component mixture in a continuum bath of solvent. Although the actual limit $y \to 0$ is perhaps pathological, at small but finite y there is still an unexpected short range structure. The large contact value of the radial-distribution function suggests that the particles "stick" together. An interesting analogy can be made with Baxter's "sticky sphere" model [24], which has an inter-particle potential defined as:

$$
\begin{aligned}
\beta v(\mathbf{r}) = & \quad +\infty & 0 < \sigma', \\
= & \quad \log[12\tau\frac{(\sigma - \sigma')}{\sigma}] & \sigma' < \mathbf{r} < \sigma, \\
= & \quad 0, & r > \sigma \quad (2.16)
\end{aligned}
$$

Then $\sigma' - \sigma$ is allowed to become infinitesimally small. Surprisingly enough, this model can also be solved in the PY approximation. It then has a critical point and shows other behavior reminiscent of a realistic fluid system with attractive interactions. In the low-density limit $g \overset{\rho\to 0}{\sim} \exp[-\beta v]$ so that in this case the

[5] Note that most previous authors worked with constant number fractions. Lebowitz and Rowlingson do this as well when they take the limit $y \to 0$. The distinction between constant number density and constant volume fraction is crucial!

contact value of the radial distribution function diverges as:

$$g \overset{\rho \to 0}{\sim} \frac{\sigma}{12\tau(\sigma' - \sigma)} \sim \frac{1}{z} \ , \ z = (\sigma' - \sigma)/\sigma \to 0 \tag{2.17}$$

In a first approximation, the potential between the large particles is the same as (2.16) with :

$$\begin{aligned} \tau &= \frac{(1 - \eta_1 - \eta_2)^2}{18\eta_1} \ and \\ (\sigma' - \sigma) &= \sigma_1 \end{aligned} \tag{2.18}$$

In the PY approximation the critical point is found at $\tau_c = (2 - \sqrt{2})/6$ and $\eta_c = (3\sqrt{2} - 4)/2$. Using:

$$\begin{aligned} \eta_1 &= 1 + \frac{9\tau}{(1 - \eta_B)^2} - \frac{\{18\tau + 81\tau^2/(1 - \eta_B)^2\}^{1/2}}{1 - \eta_B} \\ \eta_2 &= (1 - \eta_1)\eta_B \end{aligned} \tag{2.19}$$

where η_B is the renormalized effective density of the Baxter Model. The critical η_1 and η_2 are found to be 0.249 and 0.0912 respectively. This approach holds best for the limit $y \to 0$ although it may still give an indication of where to look for finite y when a better approximation than (2.19) is be used for the effective η_2

Another way of looking at the net attraction is in terms of the "osmotic depletion" effect [25, 26]. This semi-quantitative argument uses the fact that when two large spheres are closer than $\sigma_2 + \sigma_1$, the small spheres can't penetrate between the large ones, causing a pressure imbalance that pushes the two large spheres together. The pressure is assumed to be caused by the small particles only and they don't feel each other. A simple geometric argument [21] shows that when the spheres get close together, the number of expelled small spheres goes as $\frac{1}{y}$. Of course these (two-body) arguments are over-simplified, as the small particles do feel each other and the interparticle forces are of a many-body nature. As y gets smaller though, the 2-body approximation should keep getting better. This holdsfor the 2-body Baxter interaction as well. The depletion effect was originally introduced to explain demixing and flocculation of polymer-colloid mixtures. The polymers are taken to be small interpenetrable spheres with a diameter roughly equal to their radius of gyration. As the polymers get longer, the two-body assumption breaks down [28], but for short polymers, the arguments work very well. For the binary hard-sphere mixture, the interpenetrability approximation also breaks down, but if there really is an attraction between large particles of the type derived above, certainly the mechanism must be some version of the depletion effect.

The unexpected behavior in the $y \to 0$ limit (with the volume fractions held fixed!) is of some interest for colloidal suspensions where the approximation is often made that the large colloidal particles are an effective one-component mixture. In their article [21], Biben and Hansen consider this to be peculiar to the hard-sphere model, as all kinds of energetic interactions are neglected there.

Of course an obvious criticism of (2.15) would be that all the above is just an artefact of the PY approximation, but other more sophisticated "thermodynamically consistent" approximations like RY give even larger values of the contact $g_{22}(\sigma_2)$. For a size ratio y of 0.1, this can be an order of magnitude more than the PY result [6].

The net attraction between the hard-spheres at larger size ratio's than previously considered [17, 18] raises the possibility of phase separation again, and in a series of articles [22, 23, 30] Biben and Hansen have investigated this. Phase separtion is heralded by a divergence in the long wavelength component of the concentration-concentration structure factor, which can be written as:

$$\lim_{k\to 0} S_{cc}(k) = \lim_{k\to 0} \frac{1}{N} < \rho^c_k \rho^c_k >= \frac{NkT}{(\delta^2 G^M/\delta x_1^2)_{N,P,T}} \tag{2.20}$$

where $\rho^c_k = x_2\rho^1_k - x_1\rho^2_k$, x_i is the mole fraction of component i, and G^M is the Gibbs free energy of mixing. Clearly the divergence of $S_{cc}(0)$ is equivalent to finding an inflection point in the Gibbs free energy of mixing. Using numerical techniques to solve the integral equations, Biben and Hansen calculated the related function:

$$\Lambda = \frac{x_1 x_2}{S_{cc}(k=0)} \tag{2.21}$$

for various size ratio's, and using several integral closures [7]. (see figure(2.1))

The calculations are done at a fixed η_1', which is an effective small particle packing fraction. Although the PY closure predicts an effective attraction between large particles, this is not enough to give rise to a spinodal instability. Several of the other closures do predict phase separation though, as can be clearly seen in figure(2.1). However, they do differ as to the strength and position of the divergence, which leads to the criticism that the divergence is an artefact of the integral equations used. In [23] more careful calculations are done of $S_{cc}(k)$ as can be seen in figure(2.2) The PY and RY results are almost indistinguisable except at very small k, where the divergence only occurs in the RY closure. By using the Mansoori equation of state [19] they could calculate Λ at constant pressure and found that the critical reduced pressure below which no phase separation occurs had to lie in the region $0.01 < p^* < 0.1$ for $y = 0.1$.

[6] Note that because the contact value only enters in the virial expression (2.8) multiplied by ρ_2^2 it doesn't contribute very much to the pressure at constant $\eta' s$ but small y, which explains why the PY pressure is still rather accurate.

[7] If G^M is written in the usual random mixing form $G^M/Nk_BT = (x_1 \log x_1 + x_2 \log x_2) + \beta\epsilon x_1 x_2$, with ϵ the interchange or exchange energy [1], then $\Lambda = 1 - 2x_1x_2\beta\epsilon$, which is equal to unity for an ideal mixture, so that Λ is a measure of the deviation from ideality. It also immediately follwos that $\beta\epsilon$ must be greater than two for phase-separation to occur

Figure 2.1: lambda for various integral closures, taken from [22]

Figure 2.2: The Structure function is taken from [23]

From their data, it is easy to calculate the packing fractions of the species which are within the liquid regime.

The work of Biben and Hansen is not conclusive and probably a proof should be given with computer simulations, which unfortunately turn out to be quite difficult. Preliminary simulations [31] based on the Configurational Bias Monte-Carlo method (see for example [43]) with y = 0.3 seem to show that RY is superior to PY for various properties, leading to more confidence in it's predicitions of phase-separation.

If there is an instability leading to phase-separation in the fluid phase, important questions would pertain to the nature of the coexisting phases. One can think of many scenarios such as two types of crystal, fluid, glassy phases, or even a combination of any two of these coexisting. Even small differences in size can lead to very complicated behavior [48]

The last few years have seen the development of colloidal particles suspended in solution that behave nearly like hard spheres(see [50] for references), so that another way to look for phase separation is experiments on these (nearly) hard sphere systems. The first of these [49] was done with polystyrene balls of radii $0.8\mu m$ and $4.0\mu m$ in an aqueous solution. Electrolytes were added to screen the coulomb interactions between the spheres, so that the authors claim to be working effectively with a hard sphere mixture with a diameter ratio $y = 0.2$. The volume (or packing) fractions were 4:1, 1:1 and 1:4 respectively. They let the suspensions sediment, effectively increasing the colloid volume fractions. For mixtures they always see flocculation in the sediment, while this doesn't seem to occur for the pure suspensions. By adding the right concentration of $D_2 0$, they can surpress the sedimentation, and no flocculation occurs, suggesting that the higher volume fractions are crucial. From their sediment they conclude that the large particles are in a solid phase, although they don't specify if they see crystalization. The small ones are still fluid. These experiments are quite elegant in their simplicity. Unfortunately the article is a bit superficial and so there are still a lot of questions about the real hard-sphere character of their suspensions [50]. The authors claim to use a simplified density functional theory as well, but their results are for the limit of very small volume fraction of the little particles. This doesn't pertain to this experiment, and it's not really clear what density functionals have to do with their result either, although it would be very nice if that could be worked out. Much more careful and comprehensive experiments were done recently at the van 't Hoff laboratory in Utrecht[50] with sterically stabilized silica particles of radii $35nm$ and $212nm$ respectively. By adding solution, the volume fractions could be varied. If the system were to phase-separate in the fluid phase, one would expect the flocs to sediment much more rapidly. Another tell-tale sign would be a large increase in the intensity of small angle light scattering. In a limited range of volume fractions (see (figure 2.3)) they observe a sudden onset of both effects, signaling a demixing phase transition. A very careful analysis [50] of the effective interparticle interactions shows that that even these experiments aren't definitive proof of a demixing

Figure 2.3: Phase separation is shown by the triangles

transition in an additive hard-sphere mixture. It should be noted that even a slight non-additivity is known to drive phase separation [52, 53]. A look at the figure shows the surprising result that the transition dissappears at even higher volume fractions. The reason for this is not clear. Of course if the time scale of sedimentation is shorter than that of the phase separation, it would mean that the system simply hasn't reached the equilibrium time regime yet. However one could also think of other, perhaps more exotic, kinetic effects. The sediment of large particles forms an ordered crystal if you wait long enough. This is extremely beautiful, both because one can see the crystalline order with the naked eye, and because the bragg reflection in the visible regime leads to spectacular coloring effects. It even turns out that in some cases the mixed sediment forms a better crystal than the un-mixed sediment [51]. Certainly there is a lot more to binary hard sphere mixtures than demixing alone, as future investigations will undoubtably show.

k

Chapter 3

Simple Lattice Models of Entropic Phase Separation

3.1 An Exactly Solvable Model

The full partition function of a binary hard sphere mixture can't be calculated. However, if one retreats to a lattice, there are hard-core mixture models that can be exactly solved.

Consider an N-site d-dimensional hypercubic lattice model with at most one particle allowed per site. For such a lattice the grand canonical partition function is:

$$\Xi = \sum_{\{n_i\}} exp[\beta\mu \sum_i n_i] \tag{3.1}$$

The sum is over all allowed sets of occupation number $\{n_i\}$, and μ is the chemical potential. (The volume v_0 per cell has been set to 1 and the the integration over momentum coordinates has been absorbed into the fugacity $z = e^{(\beta\mu)}$ through the effective chemical potential). This can be solved to give:

$$\Xi = \sum_{k=0}^{N} \frac{N!z^k}{k!(N-k)!} \ = \ (1+z)^N \tag{3.2}$$

The reduced pressure is:

$$\beta p = \ln(1+z), \tag{3.3}$$

the particle number density is:

$$\rho = \frac{z}{1+z} \tag{3.4}$$

Figure 3.1: Exactly solvable lattice-gas model or a mixture of large(black squares) and small(white squares) hard particles. The crosses indicate which small-particle sites are excluded by the presence of large particles.

and the entropy is:

$$\begin{aligned} S &= \frac{E}{T} + \frac{pV}{T} - \frac{N\mu}{T} \; so\; that \\ \frac{S}{k_B} &= \ln(1+z) - \frac{z}{1+z}\ln(z) \end{aligned} \tag{3.5}$$

Now for a 2-D model, include "small" particles which are allowed to sit on the links of the lattice. These small particles are excluded from the edge of a square that is occupied by a large particle. The small particles occupy a square lattice such that their maximum number is twice that of the large particles (see figure(3.1)) For a fixed configuration of large particles n_i, one can define $M = M(\{n_i\})$ to be the number of free spaces available to the small particles. The partition function of the small particles is then of the same form as (3.1), namely:

$$\Xi_{small}(\{n_i\}) = (1+z_s)^{M(\{n_i\})} \tag{3.6}$$

where z_s is the small particle fugacity. $M(\{n_i\})$ can be written as:

$$M(\{n_i\}) = 2N - 4\sum_i n_i + \sum_{<ij>} n_i n_j \tag{3.7}$$

2N is the number of sites, the second term comes from the fact that one large particle excludes 4 small-particle sites, and the last sum is over nearest-neighbor pairs and corrects for overcounting when two large particles touch, and a small particle site is doubly excluded. The partition function for the mixture becomes:

$$\Xi_{mixture} = \sum_{\{n_i\}} \exp\left[(\beta\mu_l - 4\log(1+z_s)) \sum_i n_i + [\log(1+z_s)] \sum_{<ij>} n_i n_j \right] \tag{3.8}$$

This can be rewritten in the form:

$$\Xi_{mixture} = \sum_{\{n_i\}} \exp[(\beta\mu^*) \sum_i n_i + \beta\epsilon^* \sum_{<ij>} n_i n_j] \tag{3.9}$$

with

$$\mu^* = \mu_l - 4\ln(1+z_s)/\beta \tag{3.10}$$

and,

$$\epsilon^* = \ln(1+z_s)/\beta \tag{3.11}$$

The factor $(1+z_s)^{2N}$ has been omitted, and μ_l is the large particle chemical potential. Equation (3.9) is simply a one-component lattice gas Ising model with a shifted chemical potential (3.10) and a shifted nearest neighbor well depth (3.11) [1 2] that can be mapped onto a 2-D Ising spin model [32] with a nearest neighbor interaction:

$$J = \frac{1}{4}\ln(1+z_s)/\beta \tag{3.12}$$

and an external field:

$$H = \frac{1}{2}\mu_l - ln(1+z_s)/\beta \tag{3.13}$$

In what can only be called a great analytical "tour de force", Lars Onsager solved the Ising model for zero external field back in 1944 [33]. [3] No external field would correspond to the line [4] :

$$(1+z_s)^2 = z_l \tag{3.14}$$

[1]This mapping could be carried through with any kind of energy term $E(\{n_i\})$. The effect would still be to shift the n.n. well depth. All other energetic interactions would remain unchanged.

[2]The small particles can also be summed out to give a *very* complicated model which is now also solved through the equivalence with (3.9). An energetic n.n.interaction between small particles can be added as well, and mapped back onto the (3.9). This would give an effective $\tilde{z}_l = (1+z_l)\exp[\beta\epsilon]$ and $\tilde{z}_s = z_s \exp[2\beta\epsilon]$ However, only one of the two types of particles can have an energetic interaction at one time.

[3]Onsager's solution is very complicated. The simplest solution I know (and like) is that by Vdovichenko[36]. The most popular solution is that of Shultz et al.[37] who solve the model by transforming to a fermionic representation

[4]In general, with a d-dimensional hypercubic model with pairwise doubly excluded small particles, the case of no external field corresponds to $(1+z_s)^q/2 = z_l$ where q is the lattice coordination number. A 3-d model would be a mixture of (big) cubes and with tetrahedra on the links. It can be mapped onto the (unsolved) 3-d Ising model.

The spontaneous magnetization for zero field was calculated a few years later by C.N. Yang [35], and from it the density of large particles as a function of small particle fugacity (or large particle fugacity) along (3.14) can be calculated:

$$\begin{aligned} \frac{N_l}{V} &= \left\{ \tfrac{1}{2} \pm \frac{(2+z_s)^{\frac{1}{4}}(z_s^2-4z_s-4)^{\frac{1}{8}}}{z_s^{\frac{1}{8}}} \right\} \quad z_s > z_s^c \\ \frac{N_l}{V} &= \tfrac{1}{2} \quad if \quad z_s < z_s^c \end{aligned} \tag{3.15}$$

where $z_s^c = 2\sqrt{2}+2$ and $z_l^c = (3+2\sqrt{2})^2$ are the fugacities corresponding to the critical point. The small particle density can also be calculated from the expression of the energy of the lattice gas to give :

$$\begin{aligned} \frac{N_s}{V} &= \frac{z_s}{1+z_s}\left\{ \frac{3}{2} - 2N_l/V + \frac{1}{4}(\frac{z_s+2}{z_s}) \right. \\ & \left. [1+\frac{2}{\pi}[2(\frac{z_s}{2+z_s})^2-1]] \int_0^{\frac{\pi}{2}} \frac{d\phi}{(1-\delta^2 sin^2(\phi))^{\frac{1}{2}}} \right\}, \\ where \quad \delta^2 &= 2\frac{(1+z_s)^{1/2}-(1+z_s)^{-1/2}}{(1+z_s)^{1/2}+(1+z_s)^{1/2}} \end{aligned} \tag{3.16}$$

A standard way of presenting the phase-diagram of a mixture is to plot the temperature as a function of the mole fraction of one of the components. In fig (3.2) this has been done, except that $1/z_s$ has taken on the role of the temperature.

There is a first-order demixing transition for $z_s > z_s^c$. The line that can be exactly solved corresponds to the coexistence line. This has been denoted in figure (3.3): The circle is again the critical point located at $z_s = 2+2\sqrt{2}$, $z_l = (3+2\sqrt{2})^2$.

Both the large and small particles can only exlude one of their kind, so this model doesn't have a real fluid-solid transition. Perhaps it's nicest as a kind of simple or generic model of entropic phase separation, much like the binary mixture model found in many standard textbooks. More will be said on this in chapter 4

3.2 Extended Models

One of the important questions raised by the work of Biben & Hansen was whether or not the de-mixing transition is of the fluid-fluid or fluid-solid type. As the square-lattice binary Ising mixture doesn't have a clear solid phase, it can't answer such a question.

Figure 3.2: Phase diagram of the model system. X_l denotes the molar fraction of large squares, z_s is the fugacity of small squares. The drawn curve indicates the composition of coexisting phases. Note that this curve is asymmetric. In particular, the critical point (indicated by a black dot) is located at $X_l = \sqrt{2}-1$. Along the coexistence curve, the fugacities of the large and small particles are related through $z_l = (1 + z_s)^2$.

.

Figure 3.3: The exactly solvable line in the phase diagram. The single line corresponds to a large particle density of $\frac{1}{2}$, while the double line corresponds to the first-order demixing transition.

A model which does have a solid phase is the hard hexagon model solved by Baxter using corner-transfer matrices [39, 38]. The partition function for the one-component mixture has the same form as (3.1), but now the sum over n_i is extremely complicated. That the model must have a fluid-solid transition, or at least two phases, can be seen from figure (3.4). At low fugacities, the hexagons will be equally partitioned over the three sublattices, while for high fugacities, there will be a symmetry breaking phase where the hexagons reside mainly on one of the three sublattices.

This was rigerously proven by Baxter [39], who calculated the partition function per site for the infinite lattice:

$$\kappa = \lim_{N\to\infty} Z^{1/N}, \tag{3.17}$$

as well as the mean density:

$$\rho = (\rho_1 + \rho_2\rho_3)/3 = z(\frac{\delta}{\delta z})\ln\kappa \tag{3.18}$$

and the order parameter:

$$R = \rho_1 - \rho_2 = \rho_1 - \rho_3 \tag{3.19}$$

After doing an analysis with corner transfer matrices, he expanded the fugacity to order 30 in x, a parameter that lies between ± 1, and is a ratio of two

Figure 3.4: The lattice is split up into three sublattices. Taken from [38]

corner transfer matrix eigenvalues. Rewriting this expansion in the (trial) form:

$$z = -x \prod_{n=1}^{\infty} (1 - x^n)^{c_n}, \tag{3.20}$$

he found that c_n repeated itself as: $c_n = 5, -5, -5, 0, 5, \ldots$, so that taking k as the k^{th} repetition of the c's he easily guessed :

$$\begin{aligned} z &= -x \prod_{k=1}^{\infty} (1 - x^{5k-4})^5 (1 - x^{5k-3})^{-5} (1 - x^{5k-2})^{-5} (1 - x^{5k-1})^5 \\ z &= -x \left[\frac{H(x)}{G(x)} \right]^5 \\ & \quad with : \end{aligned} \tag{3.21}$$

$$\begin{aligned} H(x) &= \prod_{k=1}^{\infty} (1 - x^{5k-3})^{-1} (1 - x^{5k-2})^{-1} \\ G(x) &= \prod_{k=1}^{\infty} (1 - x^{5k-4})^1 (1 - x^{5k-1})^1 \end{aligned} \tag{3.22}$$

Using the same method, he also calculates κ and R to be:

$$\kappa = \frac{x^{1/3} g^3(x) Q^2(x^5)}{H^2(x)} \prod_{n=1}^{\infty} \frac{(1 - x^{3n-2})(1 - x^{3n-1})}{(1 - x^{3n})^2} \tag{3.23}$$

and

$$R = \frac{Q(x)Q(x^5)}{Q^2(x^3)} \tag{3.24}$$

where

$$Q(x) = \prod_{n=1}^{\infty} (1 - x^n) \tag{3.25}$$

He then goes on to prove his conjectures [38] in a long and complicated analysis where he actually solves a more general model, namely a hard square model with diagonal (asymmetric) interactions of strength L and M for the two-dimensional manifold

$$z = \frac{e^L e^M (1 - e^L)(1 - e^M)}{1 - e^L - e^M}. \tag{3.26}$$

Of course z must be greater than zero. This model can be shown to reduce to the hard-hexagon model in the limit $L \to 0, M \to -\infty$ Using properties of elliptic functions like those derived by Rogers and Ramanujan [40] he derives the following properies at the critical fugacity:

$$\begin{aligned} z_c &= \frac{1}{2}(11 + 5\sqrt{5}) \\ \rho_c &= (5 - \sqrt{5})/10 \\ \kappa_c &= [27(25 + 11\sqrt{5})/250]^{1/2} \\ R &= 0 \end{aligned} \tag{3.27}$$

and shows that the phase-transtion is second order. Interestingly enough, the critical point seems to be in the universality class of the three-state Potts model [54]. When the small particles are added, one can carry through exactly the same kind of mapping as in section (3.1) with

$$M(\{n_i\}) = N - 7\sum_i n_i \ + 2\sum_{<ij>} n_i n_j \ - \sum_{<ijk>} n_i n_j n_k \ + \sum_{[ij]} n_i n_j \tag{3.28}$$

$$\begin{aligned} <\text{ii}> = &\quad \text{nnn pairs} \\ <\text{ijk}> = &\quad \text{nnn triplets} \\ [\text{ ij }] = &\quad \text{nnnn pairs} \end{aligned}$$

If small particles are added as in figure (3.5), a mixture model like the previous one can be defined. The small particles are then summed out to give a partition function with more complicated interactions. In spin-language one obtains a model with an external field and multi-spin coupling:

$$\beta H \quad = \quad \beta\mu/2 + \frac{1}{4}\ln(1 + z_s)$$

Figure 3.5: A hard-hexagon mixture model. The small particles are defined so as to completely fill space if they occupy all the lattice points.

$$\begin{aligned}
\beta J_{{<}ij{>}} &= \frac{1}{4}\ln(1+z_s) \\
\beta J_{{<}ijk{>}} &= -\frac{1}{8}\ln(1+z_s) \\
\beta J_{[ij]} &= \frac{1}{4}\ln(1+z_s)
\end{aligned} \tag{3.29}$$

Together with a nearest neighbor term to account for the particle overlap constraint:

$$\begin{aligned}
&\beta J^* \sum_{i,j=nn} (\sigma_i + 1)(\sigma_j + 1) \\
&with \qquad \beta J^* \to -\infty
\end{aligned} \tag{3.30}$$

This model han't been solved yet. A related model can be defined, with particles on the links, leading to only a pairwise attraction, but it isn't clear whether this model has been solved yet either. Because the relative weights of two configurations depend only on ΔM, the change in the number of free spaces, a fast Monte-Carlo algorithm can be defined to simulate the mixture. This has been done for the model from figure (3.3). A typical snapshop of a configuration on a 99 by 99 latice is shown in figure (3.6)

Figure 3.6: A typical configuration of the hard-hexagon mixture model. The three types of particles refer to the large hexagons on the three types of sublattices. The small particles are not depicted of course.

In this case, portions of the system have "crystallized" but on different sublattices. Figure (3.7) shows some of the points calculated on a phase diagram. The lines are for a fixed small particle fugacity. For $z_s < 2$ there seems to be only a second order "freezing" transition, while for $z_s > 2$ there is a first order jump in the density which would correspond to a first-order demixing transtion. The critical point must therefore lie in the vicinty of $z_s \approx 2$ and $z_l \approx 25$. Unfortunately it turned out to be more difficult than was anticipated to map out the phase diagram. This was especially so because the second order "freezing" transition is second order, and so it is dominated by fluctuations and the simulation suffers from critical slowing down. This effect, seen in many models near a second order phase transtion is related to the large dynamic exponent. All kinds of cluster algorithms [41] have been thought up to tackle this problem. Recently Frenkel has given a very elegant and general recipe to derive these algorithms [42] which could be used to derive some one for this model. Figure (3.8) shows a conjectured phase diagram. Notice the circled part of the diagram. Even if the fluid-fluid phase coexistence cannot be found directly, it would be enough if one could calculate the critical point and the point where the second order solidification line hits the first order one. If it does so above the critical point, there must be a fluid-fluid coexistence, and if it would come in at the critical point, making this a tri-critical point, this isn't so. Of course, on such a lattice, even if one knows where the fluid-fluid transition is, the phase would perhaps be difficult to characterise. Unfortunately it turned out not to be possible to carry

Figure 3.7: phase diagram hexagons

Figure 3.8: A conjectured phase diagram for the hard hexagon mixture model.

Figure 3.9: Pase-diagram of the hard-square model. The lines III and IV are from the exactly solved line of Baxter. The thin line is the second order phase transition that is not exactly solved. This graph is from [54]

out the above program so that it is still unclear what happens in this model.

Baxter solved a generalized model for hard squares with diagonal interactions. One limit gave the hard-hexagon model. Huse [54] has shown that the parameters for which Baxter obtained a solution (3.26) also contain a line of tricritical points and a surface of first-order transitions of hard squares with attractive nearest-neighbor interactions [56]. For L = M the triciritcal point corresponds to

$$\begin{aligned} z_c =& \quad \frac{\sqrt{5}-1}{32} \\ L_c =& \quad \ln(3+\sqrt{5}) \end{aligned} \tag{3.31}$$

and Huse claims that it should be in the same universality class as the dilute Ising model. This model has been studied extensively on the Delft Ising System Processor (DISP) by M. Philippens [55], who also looked at the second order line.(see figure fig3.9)

Here again a mixture model as in figure (3.10) can be defined. When the small particles are summed out, this gives:

$$M(\{n_i\}) = N - 4\sum_i n_i + \sum_{<ij>} n_i n_j \tag{3.32}$$

Figure 3.10: The exactly solvable hard-square mixture model. Notice that there are two sub-lattices for the large squares

which looks the same as (3.7) up to a trivial factor. Of course the double sum is over nnn pairs now. This gives the same effective chemical potential and well depth as for the square lattice Ising mixture, (3.10), (3.11). The tricritical point would now correspond to:

$$\begin{aligned} z_s^c = & \quad (2+\sqrt{5})) \\ z_l^c = & \quad \frac{\sqrt{5}-1}{32}(3+\sqrt{5})^4 \end{aligned} \tag{3.33}$$

Huse claims that there is only one kind of phase transition so that the model only shows a fluid-solid phase separation. An amusing extension of the mapping is that one of the two sub-lattices can be summed out. This is in the spirit of the work of Shinomoto [14, 15] where a depletion type argument is also used for equal size particles. In essence, as the particles are identical, it doesn't really matter which of the two sub-lattices is summed out. Label one sub-lattice A, and the summed out one B. The partition function becomes:

$$\begin{aligned} \Xi &= \sum_{n_{iA}} \sum_{n_{iB}} \exp\left\{ \beta(\mu_A \sum_{iA} n_{iA} + \mu_B \sum_{iB} n_{iB}) \right\} \\ &= \sum_{n_{iA}} \exp\left\{ \beta\mu \sum_{i_A} n_{iA} + M(\{n_{i_A}\}) \ln(1+z_B) \right\} \end{aligned} \tag{3.34}$$

where

$$
\begin{aligned}
M(\{n_{i_A}\}) &= N_A - \sum_i n_{iA} + 2\sum_{<ij>} n_{iA}n_{jA} + \sum_{[ij]} n_{iA}n_{jA} \\
&- \sum_{<ijk>} n_{iA}n_{jA}n_{kA} + \sum_{<ijkl>} n_{iA}n_{jA}n_{kA}n_{lA} \qquad (3.35)
\end{aligned}
$$

$$
\begin{aligned}
<\text{ ii }> = &\quad \text{nn pairs} \\
[\text{ ij }] = &\quad \text{nnn pairs} \\
<\text{ ijk }> = &\quad \text{“triplets”} \\
<\text{ ijkl }> = &\quad \text{“quadruplets”}
\end{aligned}
\qquad (3.36)
$$

The model reduces to a square lattice Ising-Type model, but with complicated multi-spin interactions on a lattice $\sqrt{2}$ larger than the original one. In this formalism, one can even make the sublattice chemical potentials different. The hard-square model corresponds to the line $z_A = z_B$ along which one would approach the second-order symmetry breaking phase transition, which would then correspond to the (tri) critical point. As the fugacities are raised, this will probably go over to a first-order transition where the two solutions give the corresponding sub-lattice densities, so that the phase diagram probably resembles figure (3.3) in structure. Interestingly, (3.34) and (3.35) are exactly of the same form (up to a trivial constant) as the lattice-gas Ising model with small squares on the vertices instead of on the links! Note that the hard-square model has not been solved for no nnn interactions, and that the above mapping takes away the difficult excluded volume constraint. It may be possible to exactly find the critical point by a duality transform or something of that nature.

A different approach would be to to look for known energetic hard-core lattice models with a fluid-fluid transitions, and try to find mixture models that can be mapped onto them. The most recent work I could find was a review article by Runnels [57]. A look at the literature shows that the fluid-fluid transition was quite difficult to achieve. Most authors resorted either to hexagons or square models with several neighbor shells excluded. The phase diagram was determined by a transfer matrix technique on an infinitely long cylindrical lattice with a finite circumference of n sites [57]. After a number of attempts by various authors[58], Orban and Bellemans [59] succeeded in defining a model with two phase transitions which they interpreted as a fluid-fluid followed by a fluid-solid transition. Their model consisted of a square lattice with exclusion up to third neighbors, and an attraction $-g\epsilon$ for the fourth neighbors, and ϵ for the fifth neighbors. For $g = 1.2$ they find two phase transtions, one from disordered to an ordering at 5^{th} neighbor distance, and one at higher “pressure”, to a solid at 4^{th} nearest neighbor distance, which is the close-packed solid. Whether one can speak of a fluid-fluid transition is not clear, because the fifth neighbor phase is just a different solid. This shows again the previously mentioned difficulty of defining a clear fluid-fluid phase transition on a lattice. Nevertheless, one can map the above model to a mixture model. Small particles are put on the links between the large ones. A model with 4^{th} and 5^{th} neighbor attraction can be made, but not with $g > 1$, so that an additional energetic interaction must be added. The geometric interpretation of the model in terms of hard particles is also not clear. All this means that these models don't really shed any light on the hard-sphere situation. From the literature, it is clear that achieving a fluid-fluid transition in a hard lattice model is a subtle interplay of lattice size and the shape of the interaction. Even to get a first order freezing one needs to go to a third neighbor exclusion shell. To look at the effects we're interested in, it seems that the models are so complicated that they loose the inherent appeal and simplicity of the lattice. A question still open is the possibility that the method used in [57] was not sensitive enough and missed some phase transitions.

In spite of all the models defined in this section, it has not proven possible to say anything about a fluid-fluid demixing transition in these 2-D models. Of course one can easily also define 3 (or more) dimensional mixture models, and what happens there is not clear. Certainly the freezing transition will be more first-order.

3.3 Lattice Polymer Models

The mapping, or summing out of small particles is really independent of the sum over the $\{n_i\}$ of the large particles. Consider once again the model defined in (3.8) with squares [5] on a square lattice. "Polymers" can be constructed by connecting N large squares together. The sum over $\{n_i\}$ is constrained in some complicated way and all kinds of complicated lattice polymers can be made. A canonical sum for the large particles in equilibrium together with a grand canonical bath of small particles is described by the following partion function:

$$Z_{polymers} = \sum_{\{n_i\}} \exp[\frac{J}{k_A T} \sum_{<ij>} n_i n_j] \tag{3.37}$$

where $J \equiv k_B T \ln(1 + z_s)$ and the sum is over the constrained, non-overlapping or self avoiding (SAW) polymer configurations. For simple polymers this is precisely the partition function of the most-studied lattice polymer model, namely square-lattice polymers with nearest neighbor interactions. The interaction J is usually interpreted as an "exchange energy":

$$J = \epsilon = (\epsilon_{11} + \epsilon_{22}) - 2\epsilon_{12} \tag{3.38}$$

[5] or cubes in 3-D

ϵ_{ij} is the well depth of the interaction between like or unlike species. In this case (3.38) is the partition function of the Flory-Huggins (F-H) lattice model [60] which has been studied extensively both with analytical theories, in particular the well known Flory-Huggins theory [66, 67] and modifications thereof, (for a critical discussion, see the beginning of [61]) and by direct numerical simulations(see e.g. [62, 63]) [6]. These studies show that such a simple model is able to semi- quantitatively explain a wealth of different effects that are also observed experimentally. However, previous studies assumed an *energetic* interaction while in our case it is of an *entropic* origin. All results obtained for the Flory-Huggins lattice model can now be directly applied to this model. Examples are solvent induced entropic phase separation and polymer collapse. The fugacity (and of course the related (3.3) osmotic solvent pressure) plays a role similar to the inverse temperature in the energetic interpretation. It should be pointed out that the original F-H model has equal size polymeric and monomeric units. Experimental conditions are almost never like this, and one can make all kinds of size ratio's by using more small particles or by connecting hexagons or hard-squares (cubes or whatever). For the hard-square case, an extreme [7] model can be made with the polymers residing on one sublattice and the (space filling) solvent on the other. Summing out the solvent particles gives attractive interactions. A more realistic model with a polymer on one sub-lattice together with solvent, and with the other sub-lattice particles summed out leaves a Flory-Huggins type model with zero exchange energy. Frenkel and Smit [44] recently reported a very interesting sumulation of a polymer in a solvent identical to it's monomeric untis. Even in the case of repulsive interactions they see a sudden change in the dependence of the excess chemical potential on the chain length, which can be attributed to solvent induced collapse. Although the simulations are not undisputed [65], they certainly warrant additional study.

Even 50 years after it was first formulated, the Flory-Huggins theory of polymer solutions [66, 67] is still by far the most popular theory used to model such solutions. As it still defines the concepts in which people think about polymers in solution, it would be appropriate to apply it to the entropic mixture model. The derivation, which can be found in many textbooks, consists of a probabilisic (mean-field) argument to account for the polymer unit exclusion and thus does not include all kind of polymer-polymer correlations. A random mixing approximation is then made to take into account the energetic interaction and gives the following (approximate) free-energy of mixing:

$$\frac{F_{mix}}{k_A T} = \frac{\phi}{N} \log \phi + (1-\phi)\log(1-\phi) + \chi\phi(1-\phi) \tag{3.39}$$

where ϕ is the volume fraction [8] occupied by the polymer while χ is related to

[6] For 2-D polymers in the limit of long enough N collapse if z_s is 2.7. [64] Shorter polymers collapse at a higher z_s

[7] or if you wish, pathelogical

[8] In the original F-H model, all space was filled by the polymer and monomers. If that is

the exchange energy (3.38) by:

$$\chi = \frac{n_b}{2}\frac{\epsilon}{k_B T} = \frac{n_b}{2} ln(1+z_s), \tag{3.40}$$

where n_b is the coordination number of the lattice.

There have been numerous attemps to include inter and intra polymer correlations (see [61]), but as is often the case when one tries to improve on a mean field model, they have not been very successfull.

When $\chi > \frac{1}{2}$, the solvent is said to be a "poor solvent", and if it gets big enough ($\chi_c = 1/2$) demixing and collapse are likely to occur, while $\chi < \frac{1}{2}$ corresponds to a "good solvent", and the two species are miscible. Experimental results are generally fit to (3.39), to obtain a parameter χ. I f χ was purely energetic as is assumed in F-H, it would scale as $1/T$. In practice the fitted χ often has a large and dominant entropic (athermal) component. The present interperpetation of the F-H lattice model would give a completely *athermal* χ!! One can always add (attractive or repulsive) energetic interactions between the polymers and still carry out the mapping to obtain:

$$\chi = \chi_S + \chi_H, \tag{3.41}$$

a χ with an entropic (S) *and* an enthalpic (H) component in any relative ratio.

Several other theories have been proposed which give explicit entropic $\chi' s$ in incompressible polymer blends [61], and compressible polymer solutions. Schweitzer and Curro [68] have used the RISM approximation [70] to estimate the (purely entropic) χ parameter of a blend of hard-core off lattice polymers. [9]

The entropic solvent induced χ parameter proposed above (3.41) is certainly the most simple explanation of an entropic χ. None of the other theories seem to take this kind of entropy into account and concentrate on the polymer entropy alone. The solvent induced entropic component can always be added to these theories to give a more complete description of polymers in solution.

not the case, one can substitute the volume fraction of the monomers instead of $(1-\phi)$

[9] It should be noted that some predictions of their theory are still being questioned [71].

Chapter 4

Characteristics of Entropic Phase Separation.

4.1 Energy is Everything?

Textbooks on Statistical Mechanics often include a section on phase-separation in a binary lattice gas system. The two types of particles are identical but have different nearest neighbor pair-interactions so as to make the "exchange energy" ϵ (3.38) unequal to 0. This (2-D) solution is incompressible, that is to say, the particles fill the entire lattice. The model can be mapped onto an ising-spin model and solved exactly, but it is pedagogically more clear to look at it in the random mixing or Bragg-Williams approximations. The free energy of mixing is [1]

$$\begin{aligned} \frac{\Delta F^M}{Nk_BT} &= \frac{\Delta E^M}{Nk_BT} - \frac{T\Delta S^M}{Nk_BT} \\ &= \frac{c\epsilon x_1 x_2}{2k_BT} + x_1 \ln x_1 + x_2 \ln x_2 \end{aligned} \tag{4.1}$$

x_1 and x_2 are the mole fractions of the two species and c is the lattice coordination number.

The equilibrium properties of an isolated system that can exchange energy with it's surroundings are governed by the free energy $F = E - TS$ which strives to a minimum. For the binary mixture model, this means that the system is mixed for negative ΔF^M and demixed for posititive ΔF^M. As the system can't exchange particles with it's surroundings, ΔF^M only changes sign when

[1] A 'property of mixing' is the difference between that property for the mixture and the weighted average of that property for each the two pure component systems

the temperature is lowered and the energy term compensates for the negative entropy of mixing term.

The discussion above will typically be found in a chapter on order-disorder transitions. The model is often considered generic for mixtures and an illustration of how an ordered (low energy) phase competes with a disordered (high entropy) phase. The phase transition is driven by the temperature parameter so that the ("exchange") energy is the system property that crucially determines the phase behavior. The message is:

- *Energy is Everything.*

4.2 Entropy is Everything?

A popular definition of Entropy states that it is a measure of the disorder of a system. Technically it is a measure of the volume of phase space [2]. The two definitions are often compatible and a system that we consider "disordered" has a higher entropy. However, there are quite a number of cases where an apparent ordering actually corresponds to an *increase* of entropy. These counter-intuitive [3] transitions are best seen in hard-core mixtures where energy (and temperature) play no role[4]. Now the temperature plays no role, and any phase-transition will be caused by the entropy alone. These ideal systems don't exist in nature but the advent of computer simulations has made them susceptible to systematic study. The remainder of this chapter will discuss some examples of entropic phase transitions in hard-core systems.

Certainly the best known example of such a phase transtion is the solid-liquid transition of hard spheres predicted by Kirkwood in 1951 [8], and confirmed by the famous computer simulations of Alder and Wainwright in 1957 [9]. Freezing in hard sphere systems is an example of an entropic ordering transition and it's counter-intuitive nature made it controversial for many years[5].

Hard-core liquid crystal models can also exibit a wide range or ordering phase-transitions. Lars Onsager already introduced such a model in 1942 [34]

[2] In the microcanonical ensemble : $S = k_B ln\Omega$ for example. In general $S = -k \sum_j P_j \ln P_j$.

[3] Counter-intuitive will mean that the higher entropy state seems to be more ordered in the "daily life" sense.

[4] Energy does play a role of course in the sense that such a system neglects the attractive part of the potential, and approximates the repulsive part by an "effective" hard core. The kinetic energy is integrated out in the partition function to give the (ideal) thermal wavelength component. The potential energy is always the same (zero) and has no effect on the system properties. Such systems are also called a-thermal.

[5] A nice example of this can be found in [10] where Uhlenbeck is leading a discussion on the topic and takes a vote which is evenly split. Who voted for what is not listed, but among the 16 were several later Nobel-Prize winners and other "heroes" of physics. In fact Runnels says that the transition was more or less universally accepted only by about 1970 (see [57] p 315)

for hard rod like particles that could be solved exactly for infinitely thin rods and gives an entropy driven isotropic to nematic transtition. The work of Frenkel and co-workers [46] has shown that many more fascinating (partially) ordered phases can be made with entropic effects allone. Besides the nematics these include smectic and columnar phases and even a cubatic phase not yet discovered. These results, obtained mainly by creative computer simulations, are among the most spectacular of the entropic ordering transitions. Liquid crystals also ellucidate how entropy causes order. Consider Onsager's hard-rod system for example. The rods can increase their translational entropy when they form a nematic phase. If the density is high enough, this will compensate for the loss of rotational or orientational entropy. In fact, this example of entropic ordering is less non-intuitive than may seem if the previous definition is used because the ordering of spaghetti upon shaking the container is a well known "daily life" phenomenon [6]. This example demonstrates a more general phenomenon, namely that, entropic ordering occurs when there are several *"kinds"* of entropy that *"compete"* with each other much like the traditional energy-entropy competition.

Exactly solved models like Baxter's hard-hexagon model (3.3) also have entropic ordering transitions.

The topic of this thesis is entropic phase separation, and has concentrated till now on mixtures with only size differences. Interesting examples of phase-separation transitions with completely different particles exist as well. An intensely studied and technologically important one is that of colloids and non-absorbing polymers in solution. The colloidal particles will flocculate if enough polymers are added. Asakura and Oosawa first explained this entropically using a non-additive hard-sphere mixture model and the depletion effect(see (4.1)). Computer simulations [28] of a hard sphere (ideal) hard polymer mixture confirmed this model. The aforementioned competition between two types of entropy, in this case polymeric and colloidal, can be nicely illustrated in this case (see figure (4.2)).

A large (inpenetrable) colloidal particle excludes all polymer conformations that would cross it. When the interparticle distance between two (or more) colloids is less than the length of the polymer, they begin to doubly exclude some of these conformations, lowering the total number of excluded polymer conformations. If the polymer density is high enough, the increase in polymer entropy will compensate for the fact that the colloids loose entropy by staying close to each other, and the system will flocculate. The total phase diagram for the colloids even takes the form of a complete liquid with a triple point etc... but with the inverse polymer fugacity taking on the usual role of the temperature [29].

A related, but more spectacular example is the phase separation of ideal fermions and hard spheres predicted by Alavi and Frenkel [47] who exploit

[6] well, at least for pasta fans

Figure 4.1: The depletion effect. When the two large particles are close together, they exclude the shaded volume for the small particles. The arrows denote the uncompensated pressure, which, when integrated over the volume (twice) gives the potential of mean force: $-p\frac{4\pi\sigma_{12}^2}{3}(1-\frac{3r}{\sigma_{12}}+\frac{r^3}{16\sigma_{12}^3})$ taken from [26] attraction through repulsion

Figure 4.2: A schematic representation of the continuous colloidal particles and a polymer on the lattice as simulated in [28]

the well-known analogy between the Feynman path integral representation of Quantum Mechanics and ring-polymers. The path of the action functional is discretized and the functional integral is usually performed by a Monte-Carlo calculation [73]. It has been known for some years that one excess electron dissolved in a hard-sphere fluid shows a localization-delocalization transition [74]. Because of the fermi-statistics, a straightforward many-particle simulation suffers from the so-called minus-sign problem [76]. Alavi and Frenkel derived a new scheme for dealing with a non interaction many-fermion system in an arbitrary static external potential, based on a discretized [75] version of the path integral-polymer analogy. Their method does not suffer from minus-sign problems [77]. The Monte-Carlo is on the fluid configurations under influence of the directly approximated (spin-polarized) fermionic partition function. The fermions are localized in pockets in the fluid initially, much like the one-particle case. As the fermion fugacity is raised, a new phenomenon occurs and the fermions undergo a localization-delocalization transition while the fluid condenses, giving a fluid-fermion phase separation! As quantum particles are ring-polymers with an anti-symmetrization constraint, the phase-separation is not surprizing in the light of [28, 29], and can be interpreted as an entropic effect resulting from the competition between polymer and hard-sphere entropy. From an ordinary Quantum Mechanical picture, this is much more difficult to understand.

- **the binary hard-core mixture model revisited**

In spite of the plethora of entropic phase transitions, an informal survey shows that a large portion of the physics community is still ignorant of their existence. This can be partially attributed to the the lack of a simple generic type model to demonstrate some of the concepts of entropic transtions. Certainly the binary hard-core mixture model (BHCMM) described in section (3.1) could fullfill such a role, as it is simple, solvable (so it 'proves it') and has a clear (macroscopic) ordering transtition. The resemblance to the lattice-gas mixture model of section (4.1) makes it even more appealing.

Entropic phase transitions certainly aren't new, but more can be learned or demonstrated from studying such simple models. Consider the *entropy competition* for example. If the fugacities are fixed, each of the two components separately has an entropy that scales linearly with the number of spaces available for them, as can be seen from (3.5). Each of the species excludes positions for the other species, reducing it's entropy. However, the key to the ordering transition is that when one of the two species orders, it frees more volume for the other species. For the large particles, this is expressed in the sum over neighbors in (3.7) which takes into account that when two large particles touch, they doubly exclude a small one, something related to the depletion argument of figure (4.1)[7]. So, if the large particles order, they loose entropy, but in doing

[7] Notice that the entropic interaction $\ln(1 + z_s)$ is linear in the solvent pressure, just as for the the depletion interaction force,

so, they free spaces through the n.n. term, and the small particles then gain entropy. Above the critical fugacities, this gain can be so large, that the system will phase-separate, as we have shown [45].

One of the hall-marks of entropic phase transitions is that they (can) occur at a constant temperature. The nearest-neighbor interaction parameter of the (BHCMM) can include an energy term for the large particles[8] as well. Varying the temperature at constant fugacities makes the transition energetic, while varying the other way around gives entropic transitions. If there are no energetic interactions, a sign of an entropic phase transition would be an independence upon temperature!

Another hall-mark of these transitions is that they are driven by changes in composition or in (osmotic) pressure, which are both related to the fugacity (see for example (3.3) and (3.4)). Take for example one polymer in solution, in contact with a pure solution through a semi-permeable membrane. The polymer in solution model of section (3.3) can then be applied here. Increasing the (fugacity) will strengthen the effective polymer-polymer interaction, driving a collapse transiton. One can also think of this in terms of the pressure. As the solvent pressure increases, the polymer collapses to free volume for the solvent. Again, if there is an energetic interaction, one could vary both temperature and/or solvent fugacity to obtain the same collapse transtion, but from completely different mechanisms.

To conclude, clearly entropic phase transitions exist, and there is now a very simple exact generic type model to demonstrate them. The fact that the model can be mapped onto something masking as energy, or even something adding to the energy makes it especially interesting, as all kinds of energetic type phenomena can also be made entropically. The message of this section can therefore only be:

- *Entropy is Everything!* [9]

[8] or for the small ones, see the footnote following (3.11).

[9] well OK, sometimes

Chapter 5

Conclusions, Discussions and Afterthoughts.

- **Simple Lattice Models**

In chapter 3 a series of simple lattice models were developed, two of which were exactly solvable. The hard-square lattice model is more realistic than the Ising based model[45], but doesn't have it's generic appeal. The Ising lattice model is a special case of the more general class of bond-decorated Ising models. Future investigations could look at models with repulsive (= antiferromagnetic) but not hard interactions. Such models would resemble the system simulated by de Kuiper et al. [78] who showed that mixtures with an α-exp-6 interactions would phase separatate. As was emphasised in chapter 4, the most important aspect of these models is their inherent simplicity, which can be used to gain intuition for more realistic but also more complicated systems.

- **Simple Lattice Polymers in Solution**

The lattice polymer solution of chapter 3 has more important (new) physical implications than the simple mixture models do. This was demonstrated in the Flory-Huggins approximation where the famous χ parameter was shown to have a solvent-induced entropic component, which implies entropic phase-separation and collapse. It also shows that defining the θ point as a θ temperature is clearly naive, as in this model it is dependent on composition (or pressure or fugacities) so that one could even speak of a θ pressure! Things become even more complicated when energetic interactions are taken through the mapping, as the point would now depend on temperature *and* composition. In fact, depending on what is varied, the same phenomenon (collapse for instance) would be driven by energetic or entropic interactions. This should be a very general phenomenon in many kinds of polymer solutions.

- **Continuum models**

The binary hard-sphere mixture Biben and Hansen [21, 22, 23, 30] and Lebowitz and Rowlinson [16, 17] studied is closer to real physical systems than the lattice models, but unfortunately much more difficult to treat. Certainly the unexpected divergence of $g_{22}(\sigma_2)$ [21] is extremely interesting. Even if ther is no phase-separation, it warrants some more attention. In spite of their formal derivations and often good quantitative predictions, the intergral equations (PY, HNC, RY) are less than rigorous, so that if they disagree on something qualitative, it makes the question subtle indeed. The same occurs in liquid crystal models where the HNC equation sometimes predicts transitions PY misses [46]. There is some circumstantial evidence that RY results can be trusted more than PY for the hard spheres, but everything is far from definitely answered. As was the case for the original freezing transition, computer simulations will probably be needed to test for the transition and to ellucidate the composition of the coexisting phases.

In a sense, binary hard-sphere mixtures are a "worst case" and the solvent exclusion effect should be much stronger in liquid crystal models for example. Possibilities include plate like molecules or even binary mixtures of spherocylinders, which are known to phase-separate[79], although it's not clear if the best interpretation is a solvent exclusion effect. It may be possible to study such mixtures with PY like integral equation techniques. Membranes in solution should also feel a very strong solvent-induced attraction if they can get close enough to each other to overcome the entropic repulsion due to undulation forces. One membrane should also feel intramembrane attraction. Kantor, Kardar and Nelson [80, 81] have predicted a crumpling transition in the tethered membrane model they introduced. This model consists of hard-spheres attached to each other in a fixed d-dimensional network. Computer simulations suggested that this transition did not occur while recent experimental work showed that they crumple and collapse(See [82] for the experiment and references on the simulations). Enhanced membrane-affinity due to a poor solvent was used to explain this. Recent [83] simulations for a tethered membrane with a square-well potential do seem to show the behavior seen experimentally. The range of the well is such that it could also be seen as an approximation to the force expected from a depletion type argument.

The solvent-induced attraction needs to be less strong for polymer collapse than for phase-separation in the similar lattice mixture model. (z_{sc} is about half as small). Perhaps computer simulations of a entropic collapse in a hard-sphere polymer in a hard-sphere solution with $y < 1$ would be more feasible than simulations of the phase-separation in the simple mixture. This could be important for predicting experiments.

On a lattice things are well understood, but it is not obvious how the results translate (quantitatively) to the continuum case. The discussion above shows that there is a need for an appoximate continuum theory of the solvent induced entropic attraction in the various systems. A fruitfull path that would perhaps be something in the spirit of Shinomoto [14] [1] or the work of Dickman and Hall[84] for polymers. Surprizingly, the Baxter model method of section 2.2 yields a critical point right in the (small) regime where van Duijneveldt et al. find phase-separation(see figure (2.3)).

- **Experiments**

The work of Sanyal et al. [49] and van Duijneveldt et al. [50] is certainly very suggestive, although the latter, more careful experiments show that things are still quite subtle, and that kinetic effects probably play an interesting role. One of the checks of the entropic nature of the transition would be a lack of temperature dependence. The binary colloids in solution system may not be entirely ideal in this respect.

One can easily envision an experiment like that described in section (4.2) with a polymer solution and a semi-permeable membrane in a (high) pressure system. The pressure can be varied much more rapidly than the temperature and this could perhaps be used to probe the dynamics of the collapse transition. Even if the solvent induced attraction is very small, one could always prepare the temperature just above the θ point and then get collapse upon an increase in (osmotic) pressure.

- **Non-Additivity**

An important point not yet brought up is the question of non-addititvity. In the case of binary hard sphere mixtures, this translates into:

$$\sigma_{12} = (1+\Delta)\frac{\sigma_1+\sigma_2}{2} \tag{5.1}$$

Δ is the "non-additivity parameter". A famous example of such a (fluid-fluid) phase-separating model is by Widom and Rowlinson [85] where the pairpotential between like particles is zero, but unlike particles exclude each other.From their analysis (which expands in Δ), it follows that there is no phase-separation in additive mixtures. Even a Δ of 0.2 is enough to drive phase separation [52]. Basically, these models can't be given a clear geometric interpretation. The reason for the surprize of the Biben-Hansen work is that their model is addititive.

The term non-additivity is poorly chosen as non-spherical particles are by definition non-additive according to (5.1). A better way of looking at it is to

[1] Unfortunately the derivation of Shinomoto is not as rigorous as it seems on first sight. For example, one can get all kinds of equations of state if a virial equation is used. His second order correction is includes a trunctation which is not warranted. However, it can easily be shown that the second order correction the only polynomial one that will give the correct first three virial coefficients. Perhaps a more careful analysis would give a more general method. In his second article[15], he adds a van der Waals type term and finds a result close to the PY hard-sphere-van der Waals results. This is trivial of course, as he'd already shown that his equation of state was close to the PY case.

Figure 5.1: An additive lattice square model. Note that when two large particles are one lattice space from contact, they exclude up to 1.5 times the volume of a small particle.

say that each particle type should exclude equal amounts of volume for like and unlike particles. The non-additive hard-sphere model does give a good description of some physical systems like the polymer colloid mixtures, although the actual polymer-colloid interaction is additive. Two dimensional (n_i by n_i) site squares on a lattice are additive if particles of type i exclude

$$(n_i + n_j - 1)^2 \tag{5.2}$$

particles of type j. ($i, j = 1, 2$). Even though they can be given a geometric interpetation, the models of chapter 3 are not additive in this sense. This makes them less than ideal to look at the possibility of novel fluid-fluid phase separation because this is already known to exist in non-additive sphere models. To do the mapping, it is essential that the small particles only exclude one of their own kind, but two or more of the large particles. To have such an overlap, they must be on a different type of lattice making the additivity very difficult, or else they have to be bigger than one lattice site, and then the summing-out trick can no longer be applied. Figure (5.1) shows such a model. Crucial to the entropy competition is the lattice version of the depletion effect which was represented by the nearest neighbor double exclusion term in the solvable models. Notice that this double exclusion is still present, leading to the prediction of phase-separation under suitable conditions, but transition will probably be harder to reach than in the models discussed in this chapter. Simulations by Marjolein Dijkstra and Daan Frenkel are in progress to test this prediciton.

- **Final Afterthoughts:**

Although inspired by the work of Biben and Hansen, our model [45] does not shed as much light on the hard-sphere case as we would have liked. *Lattice Models of Entropic Phase-Separation* do, however, suggest that entropic attractions are a very general phenomenon, and that they should show up in a wealth of experimental situations.

Appendix :

Phase separation in the PY approximation !

Dr. Jan Dhont was so kind as to share the following results with me.

In the first figure we see his results for the virial Percus-Yevick equation (PY), Scaled Particle Theory (SPT), and results using the g(r) contact values found by Grundke, Henderson, Lee and Levesque (GHLL). The small particle volume fraction ϕ_1 was set to 0.1. The phase separation, heralded by the zero's of the determinant of the stability matrix $\mathbf{M}$, sets in for size ratio's $y \leq 1/6$. Note that Lebowitz and Rowlinson[17] only went down to the size ratio $y = 1/3$ which explains why they missed the instability. (See also the discussion at the end of chapter 2.) In the second figure, the PY-spinodals are plotted as a function of the volume fractions. Notice that the width of the spinodal region keeps getting smaller as the size ratio does.

The Percus-Yevick virial equation is considered inferior to the (stable) compressibility equation because the latter is more thermodynamically consistent[17]. The Mansoori[19] equation of state, a linear combination of the two PY equations, is the best equation known. The GHLL results are equivalent to the Mansoori equation, and they don't show the instability. Of course this puts some doubt on the correctness of the PY virial results. Nevertheless the existence of the instability is very suggestive, and important in the sense that for many years people believed otherwise.

Figure .2: The determinant of $\mathbf{M}$ as a function of large particle volume fraction ϕ_2. The small particle volume fraction is held constant. PY stands for the virial PY results, SPT stands for scaled particle theory and GLLL stands for the Grundke, Henderson, Lee and Levesque results which are equivalent to the Mansoori equation. The fractions denote the size ratio y.

Figure .3: The PY virial equation spinodals.

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[76] See Ard.A. Louis **"The minus sign problem"**, (Amolf report, to be written up.) for an extensive discussion The *minus-sign problem* is a general term for fundamental difficulties which turn up in most versions of Quantum-Monte Carlo Fermion simulations, namely that average sign of the weight of the probability measure goes to zero as $\exp[-\beta\delta]$ where δ is a constant dependent on (amongst other things,) the lowest energy levels and the system size. All accuracy is then lost in the noise. The problem seems to be fundamentally different for interacting and non-interacting systems.

[77] The Feynman path integral sum over histories can be seen as a specific way of taking the n fold iteration of a certain approximation to the Green's function of an operator. This follows from the Trotter formula. However, looking at it in this way does not have the intuitive appeal of the Feynman formulation. (see L.S. Shulman, *Techniques and Applications of Path Integration* Wiley, New York (1981) for a more complete discussion of this point). Most finite temperature Quantum Lattice Simulations start from a Trotter formula and then decouple quartic interaction terms with a Hubbard-Stratonovich (H.S.) type transformation to obtain independent electrons in an (imaginary) time dependent field. (see H. De Raedt and W. von der Linden for a very nice review in "The Monte Carlo Method in Condensed Matter Physics", (ed. K. Binder), Springer-Verlag (1992).) The electrons are then traced out and the Monte-Carlo sampling is done over the auxilerary H.S. fields. These techniques are usually used for Hubbard-type models and not to my knowledge in the field of Chemical Physics. The method of Alavi and Frenkel's can be seen as equivalent to the traced out form if the Feynman approach is seen as a way of approximating the short-time propogator in a Trotter approach. However, their application of the method is completely new, and their (independent) derivation follows the intuitively pleasing Feynman approach. It should be noted that in contrast to most Quantum Monte-Carlo schemes, their sampling is not over the quantal degrees of freedom, which are treated approximatively.

For a fuller discussion, see the previous reference which should be finished soon. (I hope)

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The many brainstroming sessions on fermions held before the (white) board with Ali and Daan were greatly enjoyed so that the following illustration seems an appropriate way to end:

The real reason Ard has finished studying:

"Ha! Louis has blown his cerebral cortex"