

# 1 Equilibrium polymerization

The idea of this section is to discuss how to write the free energy for a system in which particles interact to form transient clusters, in dilute conditions where we can assume that the equilibrium state can be approximated by an ideal gas of clusters.

## 1.1 Ideal Gas in a Nutshell

Let's start by reviewing the basic concepts of an ideal gas. The partition function is

$$Q_N = \frac{1}{N! \lambda^{3N}} \int d\vec{r}_1 \dots d\vec{r}_N \exp -\beta V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \quad (1)$$

(note:  $V(\vec{r} \dots)$  is the potential,  $V$  without argument is the volume)

$$= \frac{V^N}{N! \lambda^{3N}} = \frac{Q_1^N}{N!} \quad (2)$$

where  $Q_1 = \frac{V}{\lambda^3}$ . The Free Energy  $F$  can be written as

$$\beta F_N = -\ln Q_N = -[N \ln \frac{V}{\lambda^3} - N \ln N + N] = N[\ln \rho \lambda^3 - 1] \quad (3)$$

To evaluate the pressure, we differentiate  $\beta F_N$  finding

$$\beta P = -\frac{\partial \beta F_N}{\partial V} = \frac{N}{V} = \rho \quad (4)$$

and finally, the chemical potential  $\mu$  is

$$\beta \mu = \frac{\beta G}{N} = \frac{\beta F + \beta P V}{N} = \ln \rho \lambda^3 \quad (5)$$

and  $z = \exp \beta \mu = \rho \lambda^3$ .

Going back to the expression for  $F$  (that we will generalize later on)

$$\beta F_N = N[\ln \rho \lambda^3 - 1] = N \beta \mu - N \quad (6)$$

## 1.2 Ideal gas of clusters

$$Q = \prod_{n=1}^{\infty} \frac{Q_n^{N_n}}{N_n!} \quad (7)$$

Note that  $Q_n$  is the partition function of the cluster, i.e. the conditions for being a cluster must be satisfied. This introduces a constraint (a reduction) of the phase space  $d\vec{r}_1 \dots d\vec{r}_N$ , that we may indicate with a ' sign in the integration. While it is simple to define a cluster as a group of particles such that each particle is connected to any other particle via a sequence of bond, it is sometime less clear how to define a bonded pair. In the case of strong bonds (the one commonly found in association) or in the case of square-well like interaction, there is not much ambiguity.

$$Q_n = \frac{1}{n! \lambda^{3n}} \int' d\vec{r}_1 \dots d\vec{r}_N \exp -\beta V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \quad (8)$$

Note also that particles can be not spherical. In this case

$$Q_n = \frac{1}{n! \lambda^{3n}} \int' d\vec{r}_1 \dots d\vec{r}_N d\Omega_1 \dots d\Omega_N \exp -\beta V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N, \Omega_1, \dots, \Omega_N) \quad (9)$$

where now  $\lambda$  includes the rotational component of the integral over the kinetic energy. In these cases it is convenient to redefine  $\lambda'^3 = \lambda^3 / \int d\Omega_1$  and define a spherically averaged partition function

$$Q_n = \frac{1}{n! \lambda'^{3n}} \frac{\int' d\vec{r}_1 \dots d\vec{r}_N d\Omega_1 \dots d\Omega_N \exp -\beta V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N, \Omega_1, \dots, \Omega_N)}{\int d\Omega_1 \dots d\Omega_N} \quad (10)$$

Going back to the calculation of  $F$ , we have

$$\beta F = -\ln Q = -\sum_{n=1}^{\infty} [N_n \ln Q_n - N_n \ln N_n + N_n] \quad (11)$$

To find the cluster size distribution in equilibrium  $N_n$  this time we have to minimize  $\beta F$  under the constraint  $\sum_n n N_n = N$ . Introducing a Lagrange multiplier  $\alpha$ , we get

$$\frac{\partial(\beta F + \alpha \sum_k k N_k)}{\partial N_n} = 0 \quad (12)$$

$$\ln \frac{N_n}{Q_n} - n\alpha = 0 \quad (13)$$

or

$$N_n = Q_n (\exp \alpha)^n \quad (14)$$

Since  $N_1 = Q_1 \exp \alpha$ , the same expression can be written as

$$N_n = Q_n \frac{N_1^n}{Q_1^n} = Q_n z^n \quad (15)$$

since  $\rho_1 = z$

The resulting free energy is

$$\beta F = - \sum_{n=1}^{\infty} [N_n \ln Q_n - N_n \ln Q_n \frac{N_1^n}{Q_1^n} + N_n] = - \sum_{n=1}^{\infty} [n N_n \ln \frac{N_1}{Q_1} + N_n] = N \ln N_1 / Q_1 - \#_c \quad (16)$$

where  $\#_c$  is the total number of clusters in the system. Since  $Q_1 = V/\lambda^3$  and  $\ln N_1/Q_1 = \ln \rho \lambda^3 = \beta \mu$ , the free energy, in the ideal gas of cluster approximation, can be written as

$$\beta F = N \beta \mu - \#_c \quad (17)$$

which is reminiscent of the ideal gas relation  $\#_c = \beta P V$ . Note that the monomer concentration (which fix the value of  $\mu$ ) and the total number of clusters are the only information we need to write down the system free energy.

## 2 A case study: SW and KF

To warm up, let's evaluate the partition function for the monomer (setting  $\lambda^3 = 1$ )

$$Q_1 = V \quad (18)$$

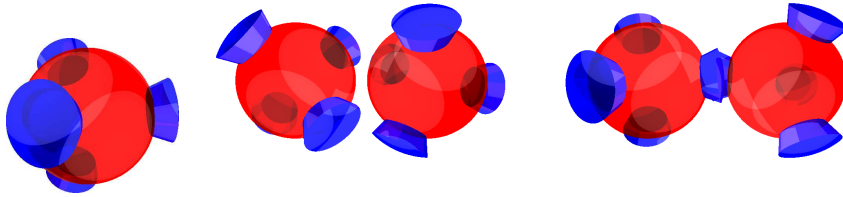
If we assume that the interaction potential is a square well, with range  $\Delta$  and depth  $-u_0$  ( $u_0 > 0$ ) then in calculating  $Q_2$

$$Q_2 = \int d\mathbf{r}_1 d\mathbf{r}_2 e^{-\beta V(\mathbf{r}_{12})}$$

we have a term  $V$  from the center of mass coordinate of the first particle and a  $V_b = \frac{4}{3}\pi[(\sigma+\Delta)^3 - \sigma^3]$  that measure the volume over which the two particles are bonded

$$Q_2 = \frac{V}{2} V_b \exp(\beta u_0) \quad (19)$$

In the case of the Kern-Frenkel potential, where bonding exists if the condition for SW are satisfied and if in addition angular constraints are satisfied (cone of semiopening  $\theta$ )  $V_b^{11} = \frac{4}{3}\pi[(\sigma + \Delta)^3 - \sigma^3]\chi^2$  where  $\chi$  is the coverage, i.e. the fraction of surface defining a patch  $\chi = \frac{1-\cos\theta}{2}$ .



Pictorial representation of a  $f = 4$  Kern-Frenkel particle (left), in a non-bonded dimer configuration (center) and in a bonded one (right)

If there are  $f$  patches on the particle,

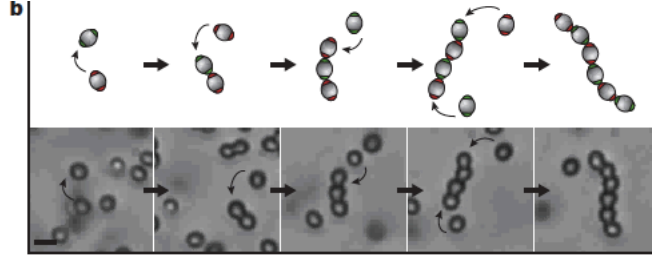
$$Q_2 = \frac{V}{2} V_b^{11} f^2 \exp(\beta u_0) \quad (20)$$

### Theory $f = 2$

Several interesting experimental systems are described by equilibrium polymerization, when aggregating particles form chains of independent bonds

# Colloids with valence and specific directional bonding

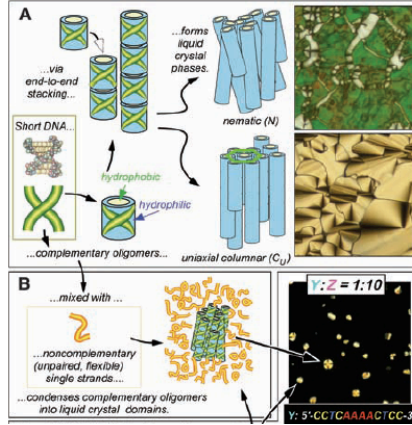
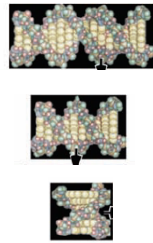
Yufeng Wang<sup>1</sup>, Yu Wang<sup>2</sup>, Dana R. Bredt<sup>2</sup>, Vinodhan N. Manoharan<sup>3,4</sup>, Lang Feng<sup>5</sup>, Andrew D. Hollingsworth<sup>1</sup>, Marcus Weickl<sup>1</sup> & David J. Pine<sup>2</sup>



La Sapienza  
Università degli Studi di Roma



**End-to-End Stacking and Liquid Crystal  
Condensation of 6 to 20 Base Pair DNA Duplexes**  
Michi Nakata, et al.  
*Science* **318**, 1276 (2007);  
DOI: 10.1126/science.1141111



La Sapienza  
Università degli Studi di Roma

For the case  $f = 2$ , the partition function ( $\lambda' = 1$ )

$$Q_n = \frac{1}{n!} \frac{\int' d\vec{r}_1 \dots d\vec{r}_N d\Omega_1 \dots d\Omega_N \exp -\beta V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N, \Omega_1, \dots, \Omega_N)}{\int d\Omega_1 \dots d\Omega_N} \quad (21)$$

can be simplified as

$$Q_n^{f=2} = \frac{\omega_n}{n!} V [V_b^{11} \exp(\beta u_0)]^{\#_b} \quad (22)$$

with  $\#_b = n - 1$

To understand how to go from one to the next, one need to "color" the particles and build the cluster. The first particles can be anywhere in the volume ( $V$ ), the second one can be in one of the two volumes  $V_b$  around the first particle and so on, up to the last one. This explain the contribution  $V[V_b^{11} \exp(\beta u_0)]^{\#b}$ . The term  $\omega_n$  measure the number of different particle arrangements that generate a bonded state

To calculate  $\omega_n$  one considers that the first particle can be selected in  $n$  ways and that it has two possible bonding configurations. The second one among the  $n - 1$  remaining particles, always with two bonding possibilities. Then we have to divide by two to account for the fact that the same chain is generated starting from one of the two ends.

$$\omega_n = \frac{2n \times 2(n-1) \times 2(n-2) \times \dots \times 2}{2} = n! 2^{n-1}$$

so that

$$\frac{\omega_n}{n!} = 2^{n-1} \quad (23)$$

One simple way to check is to label the bonding sites with letters and write down all possible distinct chains. For two particles, the first with site A and B and the second one with sites C and D one get the four possible configurations

$$AB - CD \quad BA - CD \quad AB - DC \quad BA - DC$$

and we should not include terms like  $DC - AB$  since they are identical to  $BA - CD$ .

Hence the partition function is

$$Q_n^{f=2} = 2^{n-1} V[V_b^{11} \exp(\beta u_0)]^{n-1} = V[2V_b^{11} \exp(\beta u_0)]^{n-1} \quad (24)$$

This expression has a simple interpretation:  $V$  is the center of mass partition function and  $[2V_b^{11} \exp(\beta u_0)]$  the partition function of a bond. In a chain of  $n$  particles there are  $n - 1$  bonds. Often one find defined a bond free energy as

$$\boxed{e^{-\beta \mathcal{F}_b} = 2V_b^{11} \exp(\beta u_0)}$$

so that

$$Q_n^{f=2} = V[e^{-\beta \mathcal{F}_b}]^{n-1}.$$

The cluster size distribution is given by

$$N_n = \frac{N_1^n}{Q_1^n} Q_n = \rho_1^n V [e^{-\beta \mathcal{F}_b}]^{n-1} = N_1 [\rho_1 e^{-\beta \mathcal{F}_b}]^{n-1}$$

We can also find interesting to provide a more physical (or geometrical) interpretation of the cluster size distribution. Let's start by defining the bond probability  $p_b$  as the probability that a random

site in the system is bonded as the ratio between the number of bonded sites in the system  $2\#_b$  and the total number of sites in the system  $2N$ . Then

$$p_b = \frac{2\#_b}{2N}$$

The total number of bonds in the system is  $\sum_n (n-1)N_n$ , and hence

$$\sum_n (n-1)N_n = N - \sum_n N_n = N - N_1 \frac{1}{1 - [\rho_1 e^{-\beta \mathcal{F}_b}]}$$

$$p_b = 1 - \frac{N_1}{N} \frac{1}{1 - [\rho_1 e^{-\beta \mathcal{F}_b}]}$$

Now, it is easy to convince yourself that the number of monomers are given in term of  $p_b$  by  $N_1 = N(1 - p_b)^2$ , since a monomer must have a two unbonded sites. Hence  $\rho_1 = \frac{N_1}{V} = \rho(1 - p_b)^2$

$$\frac{(1 - p_b)^2}{1 - [\rho(1 - p_b)^2 e^{-\beta \mathcal{F}_b}]} = 1 - p_b$$

$$1 - p_b = 1 - [\rho(1 - p_b)^2 e^{-\beta \mathcal{F}_b}]$$

or

$$\frac{p_b}{(1 - p_b)^2} = \rho e^{-\beta \mathcal{F}_b}$$

In this language

$$N_n = N(1 - p_b)^2 [p_b]^{n-1} \tag{25}$$

Check  $\sum n N_n = N \frac{(1-p_b)^2}{p_b} \sum n p_b^n = N$

Hence we have an exponential decay of the cluster size distribution, with characteristic size  $1/\ln p_b$ , diverging when  $p_b \rightarrow 1$ :

$$N_n = N \frac{(1 - p_b)^2}{p_b} e^{n \ln p_b} \tag{26}$$

We also note on passing that the expression

$$\boxed{\frac{p_b}{(1 - p_b)^2} = \rho e^{-\beta \mathcal{F}_b}} \tag{27}$$

could have been obtained by using the relation

$$N_2 = Q_2 \frac{N_1^2}{V^2}$$

considering that  $N_1 = N(1-p_b)^2$  and  $N_2 = N\Omega_2 p_b(1-p_b)^2$ . The value of  $\Omega_2$  can be calculated with simple consideration. A dimer is found by selecting randomly a particle ( $N$ ), by selecting randomly one of the two sites (2), by bonding it with another particle ( $p_b$ ), by imposing that all remaining sites are empty  $(1-p_b)^2$ . The final result has to be divided by two to account for the probability of starting on the second particle and re-generating the same dimer. Then  $N_2 = Np_b(1-p_b)^2$ , i.e.  $\Omega_2 = 1$ . Since  $Q_2 = \frac{4}{2!}VV_b e^{\beta u_0}$  we can write

$$Np_b(1-p_b)^2 = \frac{4}{2!}VV_b e^{\beta u_0} \frac{N^2(1-p_b)^4}{V^2}$$

or

$$\frac{p_b}{(1-p_b)^2} = \rho 2V_b e^{\beta u_0}$$

The simplex expression for the density and  $T$  dependence of  $p_b$  can be obtained by substituting  $y = \frac{1}{1-p_b}$  so that

$$\frac{1-(1-p_b)}{(1-p_b)^2} = y^2 \left(1 - \frac{1}{y}\right) = y^2 - y = \rho 2V_b e^{\beta u_0}$$

whose solution is

$$y = \frac{1 \pm \sqrt{1 + 4\rho 2V_b e^{\beta u_0}}}{2} \rightarrow 1 - p_b = \frac{2}{1 + \sqrt{1 + 8\rho V_b e^{\beta u_0}}}$$

(where we have selected the positive solution since  $0 < p_b < 1$ ) or

$$p_b = 1 - \frac{2}{1 + \sqrt{1 + 8\rho V_b e^{\beta u_0}}}$$

It is important to note that  $p_b$  depends on  $T$  and  $\rho$  via the combined term  $\rho e^{\beta u_0}$ . Hence state points with different  $T$  and  $\rho$  can behave similarly when  $\rho e^{\beta u_0}$  has the same value. More specifically, along any path in the  $T - \rho$  plane described by the function

$$\log \rho = -\frac{u_0}{k_B T} + \text{constant}$$

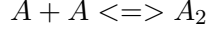
the polymerization will be identical.



The low  $T$  limit is

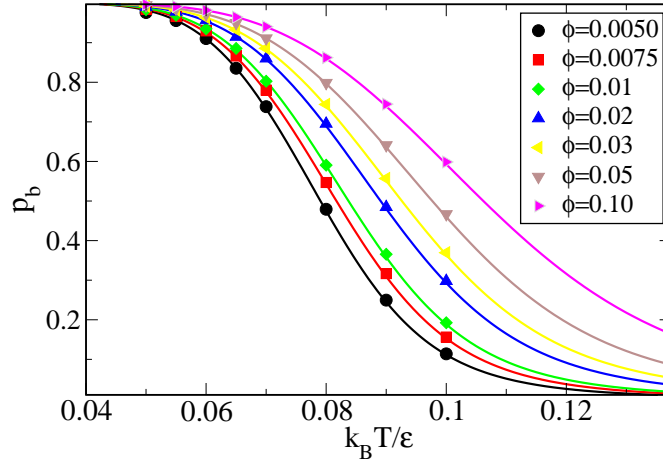
$$p_b(T \rightarrow 0) = 1 - \frac{e^{-\beta u_0/2}}{\sqrt{2\rho V_b}}$$

The same expression can be interpreted as a chemical reaction between two sites



in which  $\rho 2V_b e^{\beta u_0} \equiv \rho e^{-\beta \mathcal{F}_b}$  plays the role of free energy change from a free state in which the volume per particle is  $V/N$  to a bonded state in which the volume is  $V_b$  and the energy is  $u_0$ .  $\rho e^{-\beta \mathcal{F}_b} = \frac{2NV_b}{V} e^{\beta u_0}$ . The entropy change is the ratio between the total volume for bonding and  $V$ , while the energy change is  $u_0$ .

Since the system energy  $E = -u_0 \#_b = -u_0 p_b N$ , the  $T$  and  $\rho$  dependence of  $p_b$  is the same as the one of the potential energy. Along an isochore,  $p_b$  has a sigmoidal shape, going from zero at high  $T$  to one at low  $T$ . The  $T$ -dependence of the energy is just the opposite, going from zero at high  $T$  to  $-Nu_0$  at low  $T$ .



The fact that the energy is bounded has a relevant consequence on the behavior of the constant volume specific heat, that must show a maximum at a finite  $T$ . The presence of a peak in  $C_v$  is an hallmark of equilibrium polymerization and the locus in the  $T - \rho$  plane separates a region where the system can be considered composed by isolated monomers from a region where polymerization is relevant.

Once the cluster size distribution of chains is known, it is possible to calculate the average chain length  $L$  as

$$L \equiv \frac{\sum_{n=1}^{\infty} n N_n}{\sum_n N_n} = \frac{\sum_{n=1}^{\infty} n [p_b]^{n-1}}{\sum_n [p_b]^{n-1}} = p_b \frac{d}{dp_b} \ln \sum_n [p_b]^n = p_b \frac{d}{dp_b} \ln \frac{p_b}{1-p_b} = p_b \frac{1-p_b}{p_b} \frac{(1-p_b) + p_b}{(1-p_b)^2} = \frac{1}{1-p_b} \quad (28)$$

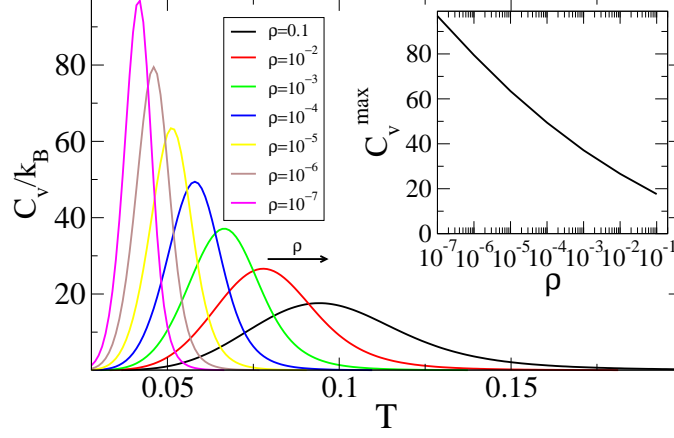


Figure 1: Predictions for the  $T$ -dependence of the specific heat  $C_V$  for different values of densities  $\rho$ . The inset shows the value of the specific heat at the maximum  $C_V^{max}$ .

Thus,

$$L = \frac{1 + \sqrt{1 + 8\rho V_b e^{\beta u_0}}}{2} \quad (29)$$

At high  $T$ ,  $L \rightarrow 1$ , while at low  $T$ ,

$$L = \frac{\sqrt{2\rho V_b} e^{\beta u_0/2}}{2}$$

and hence  $L$  grows in density as  $\sqrt{\rho}$  and in  $T$  as  $L \sim e^{\beta u_0/2}$ .

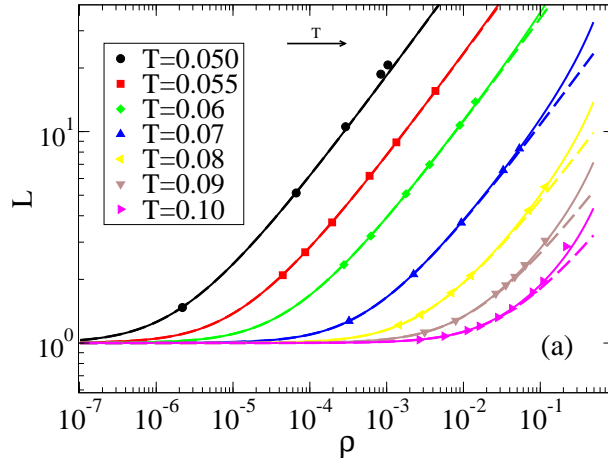


Figure 2: Average chain length as a function of the density for several temperatures.

**Identical particles with  $f$  patches - Limited valence particles**

Let's now discuss how the previous formal information can be applied to the case of single-bond-per-patch cases (limited valence particles), when there are  $f$  patches per particle and under the assumption of independent bonds...

Assuming no loops and independent bonds the general expression is

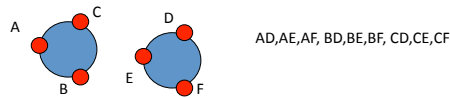
$$Q_n = \frac{\omega_n}{n!} V [V_b^{11} \exp(\beta u_0)]^{\#_b} \quad (30)$$

where  $\#_b = n - 1$  is the number of bonds and  $\omega_n$  is the number of independent bonding configurations (the permutations of all distinct  $\mathbf{r}_1 \dots \mathbf{r}_n, \Omega_1 \dots \Omega_n$  in the integral of  $Q_n$ , i.e. colored particles and colored bonding sites). In the absence of bond loops, the system partition function can be written in term of the total number of bonds in the system  $\#_{bT} = N - \#_c$

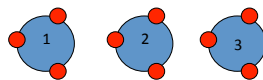
$$Q = \prod_n \frac{Q_n^{N_n}}{N_n!} = [V_b^{11} \exp(\beta u_0)]^{\#_{bT}} \prod \frac{1}{N_n!} \left(\frac{\omega_n}{n!}\right)^{N_n} \quad (31)$$

It is easy to see that  $\omega_1 = 1$  and  $\omega_2 = f^2$ . For  $n = 3$  and  $f = 3$  one can consider that there are 3 ways of forming a dimer, each with 9 possibilities. Each dimer has four open sites that can bond with the  $f$  sites. Then we have to divide by two to account for identical configurations generated via this process. The following figure explains the total counting.

$$f = 3, N = 2, \omega_2 = 9$$



$$f = 3, N = 3, \omega_3 = 162$$



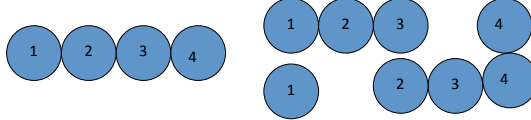
3 different dimers (12,13,23) each of them made in 9 ways, times 4x3 ways to mix a dimer with the remaining monomer, divided by two to avoid overcounting

$$3 \times 9 \times 4 \times 3 / 2 = 162$$

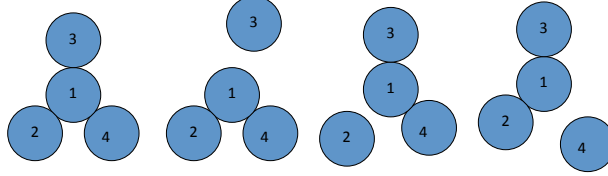
$$f = 3, N = 4, \omega_4 = 4536$$

4 different trimers (123,124,134,234), each of them made in 162 ways. Separating the linear and the star configurations one gets:

Linear configurations: times 4x3 (bonds, 4 on the trimer and 3 on the monomer) ways divided by two to avoid overcounting:  $4 \times 162 \times 4 \times 3 / 2 = 3888$



Star configuration: times 1x3 (bonds, 1 on the central particle and 3 on the monomer) divided by three to avoid overcounting  $4 \times 162 \times 1 \times 3 / 3 = 648$ .



Stockmayer (JCP 11,1945) has shown that the general expression for  $\omega_n$  is

$$\omega_n = \frac{f^n (fn - n)!}{(fn - 2n + 2)!} \quad (32)$$

resulting in

$$N_n = N_1^n \frac{Q_n}{Q_1^n} = N_1^n \frac{Q_n}{V^n} = \frac{N_1^n}{V^n} \frac{f^n (fn - n)!}{n! (fn - 2n + 2)!} V [V_b^{11} \exp \beta u_0]^{n-1} \quad (33)$$

By grouping the terms in power  $n - 1$ ,

$$N_n = N_1 \frac{f (fn - n)!}{n! (fn - 2n + 2)!} [f N_1 V_b^{11} \exp \beta u_0 / V]^{n-1} \quad (34)$$

For example,  $N_2 = N_1 f [f N_1 V_b^{11} \exp \beta u_0 / 2V]$

Now, for a better understanding, let's define  $1 - p_b$  the probability that an arbitrary patch is not bonded. Clearly, then the number of monomers is  $N_1 = N(1 - p_b)^f$ . Also, considering that in the no-loop approximation the number of bonds in a cluster of size  $n$  is  $n - 1$ , then — apart from geometric factors —  $N_n$  must be proportional to  $p_b^{n-1}$  and to  $(1 - p_b)^{fn - 2(n-1)}$  (the number of free sites is equal to the total number of sites  $fn$  minus the number of sites involved in bonding and each bond blocks two sites). Hence

$$N_n \sim p_b^{n-1} (1 - p_b)^{n(f-2)+2} = p_b^{n-1} [(1 - p_b)^{(f-2)}]^n (1 - p_b)^2 = [p_b (1 - p_b)^{(f-2)}]^{n-1} (1 - p_b)^f$$

This allow us to confirm that

$$N_1 = N(1 - p_b)^f$$

and identifying the contributions in powers of  $n - 1$

$$p_b(1 - p_b)^{(f-2)} = fN(1 - p_b)^f V_b^{11} \exp \beta u_0 / V \quad (35)$$

so that

$$\boxed{\frac{p_b}{(1 - p_b)^2} = f\rho V_b^{11} \exp \beta u_0} \quad (36)$$

Once more,  $p_b$  depends only on the combined quantity  $\rho e^{\beta u_0}$ , the potential energy is proportional to  $p_b$  and there is a peak in the constant-volume specific heat.

We can thus write

$$\boxed{N_n = N(1 - p_b)^f \frac{f(fn - n)!}{n!(fn - 2n + 2)!} [p_b(1 - p_b)^{f-2}]^{n-1}} \quad (37)$$

Here  $N_2 = \frac{f}{2}N(1 - p_b)^f [p_b(1 - p_b)^{f-2}] = \frac{f}{2}N[p_b(1 - p_b)^{2f-2}]$  and  $\frac{N_2}{N_1^2} = \frac{1}{2V}f^2V_b^{11} \exp(\beta u_0)$ .

One can check that  $\sum_n nN_n = N$ , but only when  $p < p_p$ .  $p_p$  signals the onset of an infinite cluster in the system and it is equal to  $1/(f - 1)$ .

The two boxed equations (Eq. 36 and 37) are particularly important, since they completely define the self-assembly process. The  $T$  and  $\rho$  dependence of the aggregation enters in  $p_b$ . Solving this expression provides  $p_b(T, \rho)$ . Plugging  $p_b$  in Eq. 37 allows us to calculate the cluster size distribution.

## Understanding Wertheim

Let's assume we are dealing with particles with valence  $f$ , all identical and with the single-bond per patch condition, and assume that all sites can bind. The maximum number of bonds that the system can form is  $N_b^{max} = Nf/2$ . If we call  $\#_b$  the number of bonds in the system, then we can define a bond probability  $p_b$  as  $p_b = \#_b/N_b^{max} = 2\#_b/Nf$ . In term of  $p_b$  the monomer number is  $N(1 - p_b)^f$ . Similarly, the total number of clusters is  $\#_c = N - \#_b$ . Indeed, each bond decreases by one the number of clusters. Hence  $\#_c = N - Nfp_b/2 = N(1 - fp_b/2)$  and

$$\beta F = N \ln[\rho(1 - p_b)^f] - N(1 - fp_b/2) = N[\ln(\rho) - 1] + N\{\ln[(1 - p_b)^f] + fp_b/2\} \quad (38)$$

This can be written in a more transparent way, separating the ideal gas component from the bonding remaining part

$$\beta F = \beta F_{ig} + \beta F_{bonding} \quad (39)$$

where

$$\beta F_{bonding} = N\{\ln[(1 - p_b)^f] + fp_b/2\} \quad (40)$$

The density and  $T$  dependence of  $p_b$  controls everything. All systems with the same valence behave in the same way if  $p_b$  is assumed as a scaling variable.

One can do a little better by adding the bonding free energy  $\beta F_{bonding}$  to the hard-sphere reference. Also, consistently, the hard-sphere radial distribution function  $g_{HS}$  modulates the bonding volume

$$V_b^{11} = \frac{\int d\mathbf{r}_{12}d\omega_1d\omega_2g_{HS}(\mathbf{r}_{12})e^{-\beta V(\mathbf{r}_{12},\omega_1,\omega_2)}}{\int d\omega_1d\omega_2} \quad (41)$$

The following figures shows the Wertheim phase diagram resulting from the above free energy and the way the percolation line, the specific heat maxima line and the coexistence lines behave.

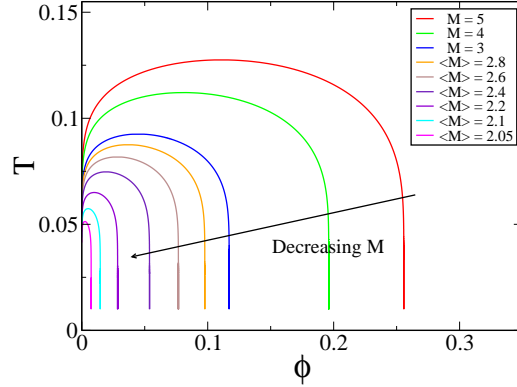


Figure 3: Spinodal curves calculated according to TPT for the studied patchy particles for several  $f = M$  and  $f = \langle M \rangle$  values.

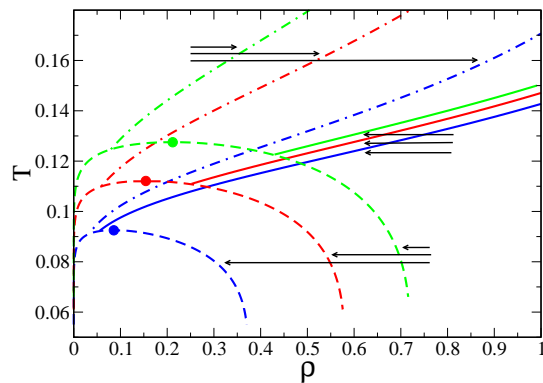


Figure 4: Theoretical predictions for the phase diagram of patchy systems on varying the particles functionality from  $f = 3$  to 5. Coexistence curves and  $C_V^{max}$  lines are evaluated according to the Wertheim theory and by finding the zeroes of the temperature derivative of  $C_V$ , i.e.  $(\partial C_V / \partial T)_V = 0$ . Percolation lines are evaluated according to the Flory-Stockmayer theory as the locus of points in the  $(T, \rho)$  plane such that  $p_b(T, \rho) = p_b^p$ .