Ideal Gas in a Nutshell

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

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

$$= \frac{V^N}{N!\lambda^{3N}} = \frac{Q_1^N}{N!} \tag{2}$$

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

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

To evaluate the pressure, we differentiate βF_N finding

$$\beta P = -\frac{\partial \beta F_N}{\partial V} = \frac{N}{V} = \rho \tag{4}$$

and finally, the chemical potential μ is

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

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

Ideal gas of clusters

$$Q = \prod_{n=1}^{\infty} \frac{Q_n^{N_n}}{N_n!} \tag{6}$$

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 $d\vec{r}_1....d\vec{r}_N$, 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.

$$Q_n = \frac{1}{n!\lambda^{3n}} \int' d\vec{r}_1 ....d\vec{r}_N \exp -\beta V(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) \tag{7}$$

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

$$Q_n = \frac{1}{n!\lambda^{3n}} \int' d\vec{r}_1 ....d\vec{r}_N d\Omega_1 ...d\Omega_N \exp -\beta V(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N, \Omega_1, ...\Omega_N) \tag{8}$$

where now λ 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

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

Going back to the calculation of F, we have

$$\beta F = -\ln Q = -\sum_{n=1}^{\infty} [N_n \ln Q_n - N_n \ln N_n + N_n] \tag{10}$$

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

$$\frac{\partial(\beta F + \alpha \sum_k kN_k)}{\partial N_n} = 0 \tag{11}$$

$$\ln \frac{N_n}{Q_n} - n\alpha = 0 \tag{12}$$

or

$$N_n = Q_n (\exp \alpha)^n \tag{13}$$

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

$$\boxed{N_n = Q_n \frac{N_1^n}{Q_1^n} = Q_n z^n} \tag{14}$$

since $\rho_1 = z$

The resulting free energy is

$$\beta F = -\sum_{n=1}^{\infty}[N_n \ln Q_n - N_n \ln Q_n \frac{N_1^n}{Q_1^n} + N_n] = -\sum_{n=1}^{\infty}[nN_n \ln \frac{N_1}{Q_1} + N_n] = N \ln N_1/Q_1 - \#_c \quad (15)$$

where $\#_c$ is the total number of clusters in the system. The free energy, in the ideal gas of cluster approximation, can always be written as

$$\boxed{\beta F = N\beta\mu - \#_c} \quad (16)$$

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

Warming up and simple definitions

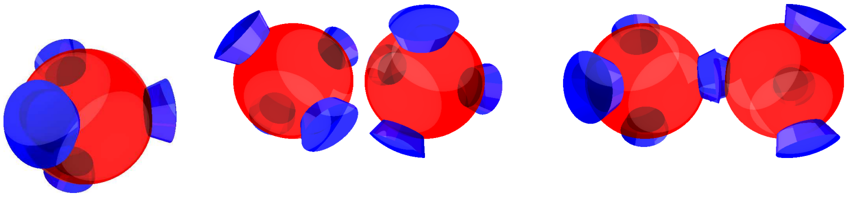
To warm up, let's evaluate the partition function for the monomer (setting $\lambda^{'3} = 1$)

$$Q_1 = V \quad (17)$$

For the dimer $Q_2 = V \int d\mathbf{r}_{12} d\omega_1 d\omega_2 e^{-\beta V(\mathbf{r}_{12},\omega_1,\omega_2)}$. If we assume that the interaction is square-well like (a potential well of depth -u_0 ($u_0 > 0$) and volume of a single patch V_b^{11} and that the particle has f patches

$$Q_2 = \frac{V}{2} f^2 V_b^{11} \exp{(\beta u_0)} \quad (18)$$

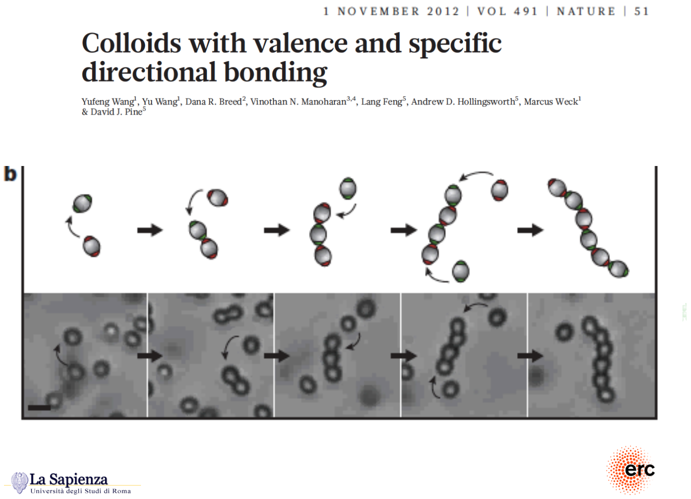
In the case of the Kern-Frenkel potential $V_b^{11} = \frac{4}{3}\pi[(\sigma + \Delta)^3 - \sigma^3)]\chi^2$ where χ is the coverage, i.e. the fraction of surface defining a patch $\chi = \frac{1-\cos\theta}{2}$.



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

Theory $f = 2$

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



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Colloids with valence and specific directional bonding

Yufeng Wang[1], Yu Wang[1], Dana R. Breed[2], Vinothan N. Manoharan[3,4], Lang Feng[5], Andrew D. Hollingsworth[5], Marcus Weck[1] & David J. Pine[5]

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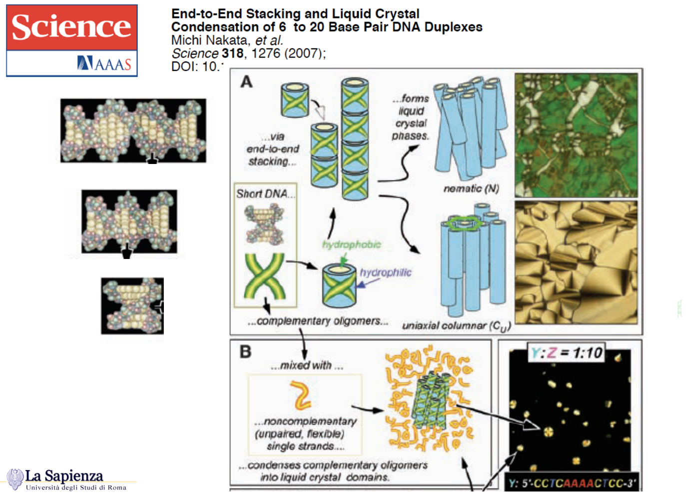


Science
AAAS

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.

La Sapienza
Università degli Studi di Roma

For the case $f = 2$, the partition function can be written as

$$Q_n^{f=2} = \frac{\omega_n}{n!} V [V_b^{11} \exp{(\beta u_0)}]^{\#_b} \tag{19}$$

with $\#_b = n - 1$ and

$$\frac{\omega_n}{n!} = 2^{n-1} \tag{20}$$

To calculate ω_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. Hence

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

Hence

$$Q_n^{f=2} = 2^{n-1} V [V_b^{11} \exp{(\beta u_0)}]^{n-1} = V[2V_b^{11} \exp{(\beta u_0)}]^{n-1} \tag{21}$$

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 $\rho_1 = \frac{N_1}{V} = \rho(1-p_b)^2$

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

or

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

In this language

$$N_n = N(1-p_b)^2[p_b]^{n-1} \tag{22}$$

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

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

$$N_n = N\frac{(1-p_b)^2}{p_b}e^{n\ln p_b} \tag{23}$$

We also note on passing that the expression

$$\boxed{\frac{p_b}{(1-p_b)^2} = \rho e^{-\beta\mathcal{F}_b}} \tag{24}$$

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 $N_2 = \Omega_2 p_b(1-p_b)^2$. The value of Ω_2 can be calculated with simple consideration. A dimer is found by selecting randomly a particle, by selecting randomly one of the two sites, by bonding it with another particle, by imposing that all remaining sites are empty. 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. This shows that $\Omega_2 = 1$. Then

$$Np_b(1-p_b)^2 = \frac{4}{2!}VV_be^{\beta u_0}\frac{N^2(1-p_b)^4}{V^2} \qquad p_b = \rho\ 2V_be^{\beta u_0}(1-p_b)^2$$

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

$$A + A <=> A_2$$

in which $\rho 2V_be^{\beta u_0} \equiv \rho e^{-\beta\mathcal{F}_b}$ 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.

Some key elements of self-assembly are already visible in the simple $f = 2$ case: The way the aggregation depends on ρ and T and the peak in the constant volume specific heat.

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, and neglecting any information on the vibrational properties of the aggregate as a whole (e.g. the polymer radius of gyration entropy) the general expression is

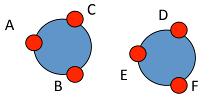
$$Q_n = \frac{\omega_n}{n!} V [V_b^{11} \exp{(\beta u_0)}]^{\#_b} \tag{25}$$

where $\#_b = n - 1$ is the number of bonds and ω_n is the number of independent bonding configurations (the permutations of all distinct $\mathbf{r}_1 ... \mathbf{r}_n, \Omega_1 .... \Omega_n$ 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 $\#_{bT} = N - \#_c$

$$Q = \prod_n \frac{Q_n^{N_n}}{N_n!} = [V_b^{11} \exp{(\beta u_0)}]^{\#_{bT}} \prod \frac{1}{N_n!} \left(\frac{\omega_n}{n!}\right)^{N_n} \tag{26}$$

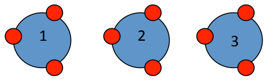
It is easy to see that $\omega_1 = 1$ and $\omega_2 = f^2$.

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



AD,AE,AF, BD,BE,BF, CD,CE,CF

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

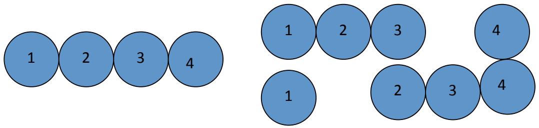


3 different dimers (12,13,23) each of them made in 9 ways, times 4x3 ways to mix a dimer with the remaining monomer, divided by two to avoid overcounting

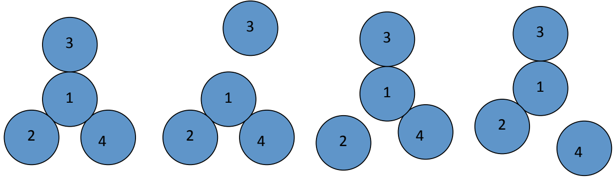
3x9x4x3/2=162

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

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 x 162 x 4 x 3 / 2 = 3888



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



Stockmayer (JCP 11,1945) has shown that the general expression for ω_n is

$$\omega_n = \frac{f^n (fn-n)!}{(fn-2n+2)!} \tag{27}$$

resulting in

$$N_n = N_1^n \frac{Q_n}{Q_1^n} = N_1^n \frac{Q_n}{V^n} = \frac{N_1^n}{V^n} \frac{f^n (fn-n)!}{n!(fn-2n+2)!} V [V_b^{11} \exp \beta u_0]^{n-1} \tag{28}$$

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

$$N_n = N_1 \frac{f(fn-n)!}{n!(fn-2n+2)!} [f N_1 V_b^{11} \exp \beta u_0 / V]^{n-1} \tag{29}$$

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 $n-1$

$$p_b(1-p_b)^{(f-2)} = fN(1-p_b)^f V_b^{11} \exp \beta u_0 / V \tag{30}$$

so that

$$\boxed{\frac{p_b}{(1-p_b)^2} = f\rho V_b^{11} \exp \beta u_0} \tag{31}$$

We can thus write

$$\boxed{N_n = N(1-p_b)^f \frac{f(fn-n)!}{n!(fn-2n+2)!}[p_b(1-p_b)^{f-2}]^{n-1}} \tag{32}$$

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 $\frac{N_2}{N_1^2} = \frac{1}{2V}f^2 V_b^{11} \exp(\beta u_0)$.

One can check that $\sum_n nN_n = N$ (when $p < p_p$). The two boxed equations (Eq. 31 and 32) are particularly important, since they completely define the self-assembly process. The T and ρ dependence of the aggregation enters in p_b. Solving this expression provides $p_b(T,\rho)$. Plugging p_b in Eq. 32 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

$$\beta F = N\ln[\rho(1-p_b)^f] - N(1-fp_b/2) = N[\ln(\rho)-1] + N\{\ln[(1-p_b)^f] + fp_b/2\} \tag{33}$$

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

$$\beta F = \beta F_{ig} + \beta F_{bonding} \tag{34}$$

where

$$\beta F_{bonding} = N\{\ln[(1-p_b)^f] + fp_b/2\} \tag{35}$$

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

$$V_b^{11} = \frac{\int d\mathbf{r}_{12} d\omega_1 d\omega_2 g_{HS}(\mathbf{r}_{12}) e^{-\beta V(\mathbf{r}_{12},\omega_1,\omega_2)}}{\int d\omega_1 d\omega_2} \tag{36}$$

To evaluate the T and ρ dependence of p_b one need to solve in term of p_b the equation for N_2,

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

Theory $f = 3$ (or larger)

When $f > 2$ ... see slides....

Exercise: Binary mixture of A$_{f_A}$ and B_{f_B} with only AB bonds

How will the bonding free energy be written in term of bond probability ? First of all, we note that the probability that a A site is bonded is $p_A = \#_b / f N_A$ and that the probability that a B site is bonded is $p_B = \#_b / f N_B$. Since $\#_b$ is the same, $p_A = p_B \frac{N_B}{N_A}$. Now....

$$\beta F = N_A \beta\mu_A + N_B \beta\mu_B - \#_c \tag{37}$$

where $\beta\mu_A = \ln(N_A(1-p_A)^{f_A})$ and $\beta\mu_B = \ln(N_B(1-p_B)^{f_B})$. The number of clusters is given, once more, by the number of particles minus the number of bonds (assuming no loops). Hence $\#_c = N_A + N_B - p_A f N_A$, or in a more symmetric way $\#_c = N_A + N_B - p_A f N_A/2 - p_B f N_B/2$.

Hence

$$\beta F = N_A \ln(N_A(1-p_A)^{f_A}/V) + N_B \ln(N_B(1-p_B)^{f_B}/V) - (N_A + N_B - p_A f_A N_A/2 - p_B f_B N_B/2) \tag{38}$$

$$\beta F = N_A \ln N_A/V - N_A + N_B \ln N_B/V - N_B + N_A[\ln(1-p_A)^{f_A} + p_A f_A/2] + N_B[\ln(1-p_B)^{f_B} + p_B f_B/2] \tag{39}$$

where the first contribution can be identified with the ideal gas contribution (including mixing entropy)

$$\beta F_{ig} = N_A \ln N_A/V - N_A + N_B \ln N_B/V - N_B = N[x \ln x + (1-x)\ln(1-x) + \ln N/V - 1] \quad (40)$$

and

$$\beta F_{bonding} = N[x(\ln(1-p_A)^{f_A} + p_A f_A/2) + (1-x)(\ln(1-p_B)^{f_B} + p_B f_B/2)] \quad (41)$$

Theory $f = 2$ competing structures ... chains and rings

(if you are interested see Quantitative description of the self-assembly of patchy particles into chains and rings J. Chem. Phys. 137, 044901 (2012))

If we assume an ideal gas of chains and rings, we can separate the cluster size distribution in two groups, chains and rings. The monomer is in equilibrium with both and hence

$$N_n^{chain} = Q_n^{chain} \frac{N_1^n}{Q_1^n} \quad (42)$$

$$N_n^{ring} = Q_n^{ring} \frac{N_1^n}{Q_1^n} \quad (43)$$

or

$$\frac{N_n^{chain}}{N_n^{ring}} = \frac{Q_n^{chain}}{Q_n^{ring}} \quad (44)$$

which means that, at the same size, the ratio between number of chains and number of rings depends only on the ratio between their partition functions. This shows that in the ideal-gas (of clusters) limit the ring size distribution is not an independent variable, being proportional to the chain size distribution times the ratio of the ring and chain partition functions.

If we define $\tilde{Q}_n \equiv Q_n/V$, the chain partition function can be written as

$$\tilde{Q}_n^c = e^{(n-1)\beta \mathcal{F}_b} \quad (45)$$

in term of the bond free energy $\mathcal{F}_b$. This expression corresponds to assume that each of the $n-1$ bonds lowers the free energy by $\mathcal{F}_b$. The ring partition function depends for short rings on the geometry of the model, while it reaches a well established asymptotic value for large n values, dictated by the self-similar nature of the growth process. More specifically, in the dilute limit,

$$\tilde{Q}_n^r \sim \frac{V_b}{n R_{ee}^3(n)} e^{n\beta \mathcal{F}_b} \tag{46}$$

where V_b is the bonding volume and R_{ee} is the end-to-end distance. Compared to linear polymers, rings are thus stabilized by the presence of n bonds (one more than a chain). On the other hand, the number of configurations allowing for ring formation are proportional to the ratio $V_b/R_{ee}^3(n)$. The additional n dependence arises from the number of way a ring can open to form a chain. Assuming that chains form a self-avoiding walk for large n (i.e. $R_{ee}(n) \sim n^{\nu_{SAW}}$, where $\nu_{SAW} = 0.588$ is the self-avoiding walk exponent), one can thus write

$$\tilde{Q}_n^r = \alpha(n) \frac{V_b}{n^{3\nu_{SAW}+1}} e^{n\beta \mathcal{F}_b} \tag{47}$$

where $\alpha(n)$ describes the model dependent short-n behavior and approaches a constant value for large n, when the self-similar nature of the chain is reached.

The system free energy can thus be expressed as

$$\beta F = N \ln N_1/V - \#_c \tag{48}$$

where

$$\#_c = \sum (N_n^{chain} + N_n^{ring}) = \sum N_n^{chain} \left(1 + \alpha(n) n^{-(3\nu_{SAW}+1)} e^{\beta \mathcal{F}_b}\right)$$

$$Q_n^{f=2} = V[2V_b^{11} \exp{(\beta u_0)}]^{n-1} \tag{49}$$

Now...

$$\sum_n N_n^{chains} = V \sum_n (\frac{N_1}{V})^n [2V_b^{11} \exp{(\beta u_0)}]^{n-1} = \frac{N_1}{1 - [2\rho_1 V_b^{11} \exp{(\beta u_0)}]}$$

$$\sum_n N_n^{chains} W_n [2V_b^{11} \exp{(\beta u_0)}] = V \sum_n W_n (\frac{N_1}{V})^n [2V_b^{11} \exp{(\beta u_0)}]^n = V \sum_n W_n [2\rho_1 V_b^{11} \exp{(\beta u_0)}]^n$$

And the free energy assumes the form

$$\beta F = N \ln \frac{N_1}{V} - \frac{N_1}{1 - [2\rho_1 V_b^{11} \exp{(\beta u_0)}]} - V \sum_n W_n [2\rho_1 V_b^{11} \exp{(\beta u_0)}]^n \tag{50}$$

In Wertheim language, since the rings do not have broken bonds, the fraction of unbonded sites $X_A = 2\sum_n N_n^{chains}/(2N)$, and X_0 is the name associated to the fraction of unbonded particles (monomers) ($X_0 = N_1/N$). In this language

$$X_A = \frac{X_0}{1 - [2\rho X_0 V_b^{11} \exp{(\beta u_0)}]}$$

The normalization condition, to evaluate N_1 arises from

$$\sum_n (nN_n^{chains} + nN_n^{rings}) = N$$

which can be expressed as

$$\frac{N_1}{(1 - [2\rho_1 V_b^{11} \exp{(\beta u_0)}])^2} + \sum_n nW_n[2\rho_1 V_b^{11} \exp{(\beta u_0)}]^n = N$$

and defining the Wertheim quantity

$$G_1 = \sum_n nW_n[2\rho_1 V_b^{11} \exp{(\beta u_0)}]^n$$

In symbolic form the normalization condition becomes

$$\frac{X_A^2}{X_0} + \frac{G_1}{\rho} = 1$$

Free energy for particles with competitive interactions

Let's discuss here the case of a particle with 2 A sites, promoting chaining and f B sites promoting branching, via AB bonds.

In this case, we can define two probabilites: the probability p_A that an A site is occupied and p_B that a B site is occupied. The monomer concentration will then be given by $N_1 = N(1-p_A)^2(1-p_B)^f$. In the system there will be N_{AA} bonds of type AA and N_{AB} bonds of type AB. In terms of these quantities we can write

$$p_A = \frac{2N_{AA} + N_{AB}}{2N} \qquad p_B = \frac{N_{AB}}{fN}$$

The probability p_A can be written as $p_{AA} + p + AB$ according to the type of bond the site is involved. Clearly $p_{AA} = N_{AA}/N$ and $p_{AB} = N_{AB}/2N$.

Inverting these relations

$$N_{AA} = Np_A - \frac{fNp_B}{2} \qquad\qquad N_{AB} = fNp_B$$

The number of clusters is always $N - \#_b = N - N_{AA} - N_{AB}$, so that

$$\beta F = N \ln \frac{N(1-p_A)^2(1-p_B)^f}{V} - N + Np_A + \frac{fNp_B}{2} =$$

$$N(\ln \rho - 1) + N \left[2\ln(1-p_A) + f\ln(1-p_B) + p_A + \frac{fp_B}{2} \right]$$

where we can easily identify the bonding contribution (per particle)

$$\beta F_{bonding}/N = 2\ln(1-p_A) + f\ln(1-p_B) + p_A + \frac{fp_B}{2}$$

To estimate the T and ρ dependence of p_A and p_b we can make use of the connection between the number of dimers and of monomers. Defining $X_A = 1 - p_A$ and $X_B = 1 - p_B$ we can immediately write

$$N_1 = NX_A^2 X_B^f$$

$$N_2^{AA} = \omega_2^{AA} N X_A^2 X_B^{2f} p_{AA}$$

$$N_2^{AB} = \omega_2^{AB} N X_A^3 X_B^{2f-1} p_{AB}$$

where $p_{AB} = \frac{f}{2}(1 - X_B)$ while

$$p_{AA} = N_{AA}/N = p_A - \frac{fp_B}{2} = (1 - X_A) - \frac{f}{2}(1 - X_B)$$

Note: $\omega_2^{AA} = 1$. Indeed a dimer can be formed by starting on any monomer N, selecting two possible sites to start the chaining (2), then connecting with probability p_{AA} and then imposing the emptiness of the other sites. Then we have to divide by 2 to avoid over-counting (selecting the final particle as the original one). For the AB case, also $\omega_2^{AB} = 1$, since we select in two ways (2) a site A and connect it to a B with probability p_{AB}. Note that we would have got the same result by selecting a B site in f ways and connecting it with an A site with probability p_{BA}. Indeed, $fp_{BA} = 2p_{AB}$.

Now, as usual,

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

which gives

$$\omega_2^{AA} N X_A^2 X_B^{2f} p_{AA} = \frac{(N X_A^2 X_B^f)^2}{V^2} Q_2^{AA}$$

and

$$\omega_2^{AB} N X_A^3 X_B^{2f-1} p_{AB} = \frac{(N X_A^2 X_B^f)^2}{V^2} Q_2^{AB}$$

Simplifying one gets

$$\omega_2^{AA} p_{AA} = \frac{N X_A^2}{V^2} Q_2^{AA} \qquad p_{AA} = \frac{N X_A^2}{V^2} \frac{Q_2^{AA}}{\omega_2^{AA}}$$

and

$$p_{AB} = \frac{N X_A X_B}{V^2} \frac{Q_2^{AB}}{\omega_2^{AB}}$$

From which we obtain the system to be solved

$$(1 - X_A) - \frac{f}{2}(1 - X_B) = \frac{N X_A^2}{V^2} \frac{Q_2^{AA}}{\omega_2^{AA}}$$

and

$$\frac{f}{2}(1 - X_B) = \frac{N X_A X_B}{V^2} \frac{Q_2^{AB}}{\omega_2^{AB}}$$

Now, $\omega_2^{AA} = \omega_2^{AB} = 1$ and one gets

$$Q_2^{AA} = \frac{1}{\omega_2^{AA}} \frac{V}{2!\lambda'^6} \frac{\int' d\vec{r}_{12} d\Omega_1 d\Omega_2 \exp -\beta V(\vec{r}_{12}, \Omega_1, \Omega_2)}{\int d\Omega_1 d\Omega_2} = 2 V V_b^{AA} e^{\beta u_{AA}}$$

where we have considered that there are 4 idential integral over AA bonds and similarly (there are $2f$ identical integrals for AB)

$$Q_2^{AB} = \frac{2f}{2!} V V_b^{AB} e^{\beta u_{AB}}$$

so that the equations to solve are

$$(1 - X_A) - \frac{f}{2}(1 - X_B) = 2 V_b^{AA} e^{\beta u_{AA}} \rho X_A^2$$

and

$$1 - X_B = 2 \rho V_b^{AB} e^{\beta u_{AB}} X_A X_B$$

Evaluation of Q_n via simulations

Work in the subspace of the cluster ($'$), i.e. the set of configurations in which all n particles belong to the same cluster.

- 1) Start from infinite T and integrate (see Fantoni et al Soft Matter)

- 2) Perform a grand canonical simulation in cluster space (see XXXX)

Let's look at the second method:

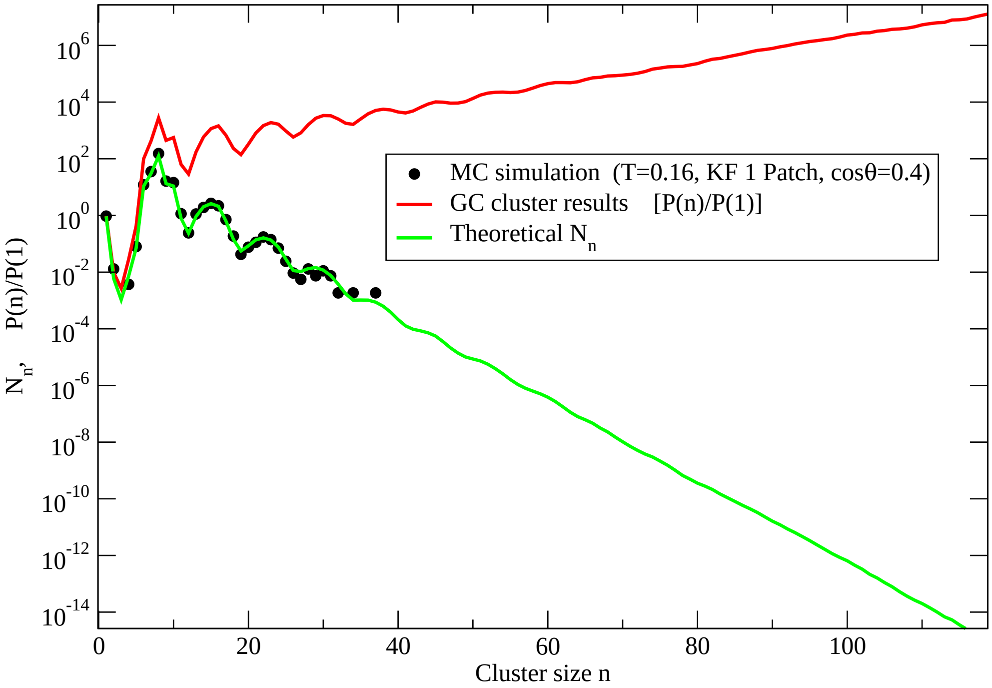
$$P(n,z,T) = \frac{z^n Q_n}{\sum_n z^n Q_n} \tag{51}$$

$$\frac{P(n,z,T)}{P(1,z,T)} = \frac{z^{n-1} Q_n}{Q_1} \tag{52}$$

$$Q_n = V \frac{P(n,z,T)}{z^{n-1} P(1,z,T)} \tag{53}$$

From here... and if one want to compare with a system with $z^{MC} = N_1/V$

$$N_n = Q_n \frac{N_1^n}{Q_1^n} = \frac{P(n,z,T)}{P(1,z,T)} \frac{N_1^n}{(zV)^{n-1}} = N_1 \frac{P(n,z,T)}{P(1,z,T)} (\frac{z^{MC}}{z^{GC}})^{n-1} \tag{54}$$



Possible numerical tricks:

- Implement umbrella sampling (even better successive umbrella sampling)
- Implement re-weighting techniques, such that in each umbrella window $P(n) \approx P(n+1)$
- Implement parallel tempering

When do we need this ....

- When the gas phase is a cluster phase !
- To evaluate coexistence with crystal phases
- To access the metastability of the gas phase