Derivations and Notes on Theory

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1 Thermodynamic Quantities to First Order in Stillinger

1.1 Partition Function with Non-Interacting Monovacancies

The general Stillinger expansion of the partition function takes the form

$$Q = \frac{1}{\Lambda^{3N}} \sum_{l} \prod_{i}^{N} Z_i^l \prod_{i<j}^{N} \frac{Z_{ij}^l}{Z_i^l Z_j^l} \cdots \tag{1.1}$$

Where the sum over l in (1.1) denotes a sum over unique injective mappings from natural numbers modulo the number of particles into the natural numbers modulo the number of lattice sites (i.e. such that for N many particles and M many lattice sites, two mappings are unique iff they do not map onto the same cardinality N subset of $\mathbb{N}/M$).

Let us again assume that we have N particles and M lattice sites. To first order in the Stillinger expansion, we include only the single particle configuration integral product, and the sum over l just reduces to a combinatorial factor counting the number of ways to place the N particles among the M lattice sites. Furthermore, let us assume that the interaction potential is finitely ranged so that only particles within n_m shells of a given particle interact with it, and let g_i be the number of particles in shell i around a fixed site. Then, for the $(M-N)$ vacancies, $(M-N)g_i$ particles "feel" the vacancy at shell i. Consequently, $\sum_i^{n_m}(M-N)g_i$ particles feel the effect of a vacancy, while $N-\sum_i^{n_m}(M-N)g_i$ do not.

For each of those particles that do not feel the effect of a vacancy, the configuration integral is identical, and is denoted Z_s. For each of those particles that feel the effect of a vacancy at shell i, the configuration integral is again identical and is denoted $Z_{sv,i}$.

Finally, this allows us to write the partition function to first order as follows:

$$\boxed{Q = \frac{1}{\Lambda^{3N}} \binom{M}{N} Z_s^{N-(M-N)\sum_i^{n_m} g_i} \prod_i^{n_m} Z_{sv,i}^{g_i(M-N)}} \tag{1.2}$$

1.2 First Order Helmholtz Free Energy

Now we examine the thermodynamic limit where $(N, M) \to \infty$ and the particle number density $\rho \equiv N/V$ (where V is the volume) is held constant. Letting the vacancy contration be given by $n_v \equiv 1 - N/M$ and using Stirling's approximation ($\ln(N!) \approx N\ln(N) - N$), we have that:

$$\frac{\beta F}{N} = \frac{-\ln(Q)}{N} \tag{1.3}$$

$$= \frac{-1}{N}\left(-N\ln(\Lambda^3) + \ln\left(\frac{M!}{N!(M-N)!}\right) + \ln(Z_s)\left(N - (M-N)\sum_i^{n_m} g_i\right) + \sum_i^{n_m} g_i (M-N)\ln(Z_{sv,i})\right) \tag{1.4}$$

$$= \frac{-1}{N}\left(N\ln\left(\frac{Z_s}{\Lambda^3}\right) + (M-N)\sum_i^{n_m} g_i \ln\left(\frac{Z_{sv,i}}{Z_s}\right) + M\ln(M) - N\ln(N) - (M-N)\ln(M-N)\right) \tag{1.5}$$

$$= -\ln\left(\frac{Z_s}{\Lambda^3}\right) - \left(\frac{n_v}{1-n_v}\right)\sum_i^{n_m} g_i \ln\left(\frac{Z_{sv,i}}{Z_s}\right) + (M/N - 1)\ln(n_v) + \ln(1-n_v) \tag{1.6}$$

$$= \boxed{-\ln\left(\frac{Z_s}{\Lambda^3}\right) - \left(\frac{n_v}{1-n_v}\right)\sum_i^{n_m} g_i \ln\left(\frac{Z_{sv,i}}{Z_s}\right) + \left(\frac{n_v}{1-n_v}\right)\ln(n_v) + \ln(1-n_v)} \tag{1.7}$$

1.3 First Order Equilibrium Vacancy Concentration

To obtain an expression for the equilibrium vacancy concentration, we must minimize the free energy per particle wrt n_v. Here, we assume that $n_v \ll 1$, and thus we only keep terms whicha are independent of or logarithmic in n_v. Thus, proceeding from equation 1.7, we have:

$$\beta \frac{\partial(F/N)}{\partial n_v} = \frac{-\Lambda^3}{Z_s}\frac{1}{\Lambda^3}\frac{\partial Z_s}{\partial n_v} - \frac{1}{(1-n_v)^2}\sum_i^{n_m} g_i \ln\left(\frac{Z_{sv,i}}{Z_s}\right) + \frac{1}{(1-n_v)^2}\ln(n_v) + \cdots \tag{1.8}$$

$$\approx \frac{-1}{Z_s}\frac{\partial Z_s}{\partial \rho}\frac{\partial \rho}{\partial n_v} - \sum_i^{n_m} g_i \ln\left(\frac{Z_{sv,i}}{Z_s}\right) + \ln(n_v) \tag{1.9}$$

$$= \frac{-1}{Z_s}\frac{\partial Z_s}{\partial \rho}\frac{\rho}{(1-n_v)^2} - \sum_i^{n_m} g_i \ln\left(\frac{Z_{sv,i}}{Z_s}\right) + \ln(n_v) \tag{1.10}$$

$$\approx -\rho\frac{Z_s'}{Z_s} - \sum_i^{n_m} g_i \ln\left(\frac{Z_{sv,i}}{Z_s}\right) + \ln(n_v) = 0 \tag{1.11}$$

$$\Rightarrow \boxed{n_{v,eq} = \exp\left(\rho\frac{Z_s'}{Z_s}\right)\prod_i^{n_m}\left(\frac{Z_{sv,i}}{Z_s}\right)^{g_i}} \tag{1.12}$$

1.4 First Order Gibb's Free Energy of Monovacancy Formation

For small $n_{v,eq}$, $\beta F \approx -N\ln\left(\frac{Z_s}{\Lambda^3}\right) \Rightarrow (F/N)' \approx -\beta^{-1}(Z_s'/Z_s)$. Since the pressure, p, is given by $p = (F/N)'\rho^2$, and using the relation $n_{v,eq} = \exp(-\beta\Delta G_v)$ (where ΔG_v is the energy of monovacancy formation), it follows directly that:

$$\boxed{\Delta G_v = \frac{p}{\rho} - \beta^{-1}\sum_i^{n_m} g_i \ln\left(\frac{Z_{sv,i}}{Z_s}\right)} \tag{1.13}$$

2 Thermodynamic Quanitites to Second Order In Stillinger

2.1 Second Order, No Vacancy Helmholtz Free Energy

In the case of no vacancies, the sum in the partition function has only one term as in this case any mapping is surjective. Therefore, in the case of no vacancies, the partition function to second order is

$$Q = \frac{1}{\Lambda^{3N}}\prod_i^N Z_i \prod_{i<j}^N \frac{Z_{ij}}{Z_i Z_j} \tag{2.1}$$

For no vacancies, each single particle integral is equivalent, i.e. in equation 1.1 we have $\forall i, j, Z_i = Z_j \equiv Z_s$. Furthermore, each two particle integral Z_{ij} where the particle with label j is in the kth shell of that with label i can be written identically as Z_{nk}. If $k > n_m$ (where n_m is defined as in 1.2), then $Z_{ij} = Z_i Z_j = Z_s^2$. Proceeding with this notation, we have:

$$\beta F = -\ln(Q) \tag{2.2}$$

$$= -\ln\left(\frac{1}{\Lambda^{3N}}\right) - \sum_{i=1}^N \ln(Z_s) - \sum_{i=1}^N\sum_{j=1}^{i-1}(\ln(Z_{ij}) - \ln(Z_s^2)) \tag{2.3}$$

$$= -N\ln\left(\frac{Z_s}{\Lambda^3}\right) + 2\frac{1}{2}N(N-1)\ln(Z_s) - \sum_{i=1}^N\sum_{j=1}^{i-1}\ln(Z_{ij}) \tag{2.4}$$

Now for each particle i (of which there are N many), there are g_k particles j in its kth shell. Note that i is then also in the kth shell of each j. This gives that there are $\frac{N}{2}g_k$ unique i, j pairs representing particles in each other's kth shell. this allows us to proceed as follows:

$$= -N\ln\left(\frac{Z_s}{\Lambda^3}\right) + (N^2 - N)\ln(Z_s) - \left(\frac{N}{2}\sum_{k=1}^{n_m} g_k \ln(Z_{nk}) + \left(\frac{1}{2}(N^2 - N) - \frac{N}{2}\sum_{k=1}^{n_m} g_k\right)\ln(Z_s^2)\right) \tag{2.5}$$

$$= -N\ln\left(\frac{Z_s}{\Lambda^3}\right) - \frac{N}{2}\sum_{k=1}^{n_m} g_k \ln(Z_{nk}) + N\sum_{k=1}^{n_m} g_k \ln(Z_s) \tag{2.6}$$

$$\Rightarrow \boxed{\frac{\beta F}{N} = -\ln\left(\frac{Z_s}{\Lambda^3}\right) - \frac{1}{2}\sum_{k=1}^{n_m} g_k \ln\left(\frac{Z_{nk}}{Z_s^2}\right)} \tag{2.7}$$

It is interesting to note that this takes the form of the one particle Helmholtz free energy per particle (c.f. equation 1.7) in the case that $n_v \to 0$, with additional corrections concerning the correlated movement of two particles at each relevant layer separation.

2.2 Second Order Helmholtz Free Energy For Hard Spheres

In the case of hard spheres, only nearest neighbor particles can interact (i.e. $n_m = 1$). Consequently, there are only two types of single particle integrals. Namely, for a particle in shell i of a vacancy, the single particle integral is Z_s if $i > 1$ or $Z_{sv,1} \equiv Z_{sv}$ otherwise.

There are, however, several types of two-particle integrals. First note that if two particles labelled i and j are separated by more than one shell, it is the case that $Z^l_{ij} = Z^l_i Z^l_j$, and consequently, $\frac{Z^l_{ij}}{Z^l_i Z^l_j} = 1$, so such cases are irrelevant. If the two moving particles are nearest-neighbors, then either neither of those two are the nearest neighbor of a vacancy (in which case we denote the two particle integral Z_{ss}), both of them are the nearest neighbor of a vacancy (in which case we denote the two particle integral Z_α), or only one of them is the nearest neighbor of a vacancy. In this final case, there are three subcases to consider. In particular, the moving particle that is not a nearest neighbor of the vacancy can be in the second, third, or fourth shell of the vacancy, where these two particle integrals will be denoted Z_δ,Z_γ, and Z_β respectively. These different cases are illustrated in figure 2.1 below.

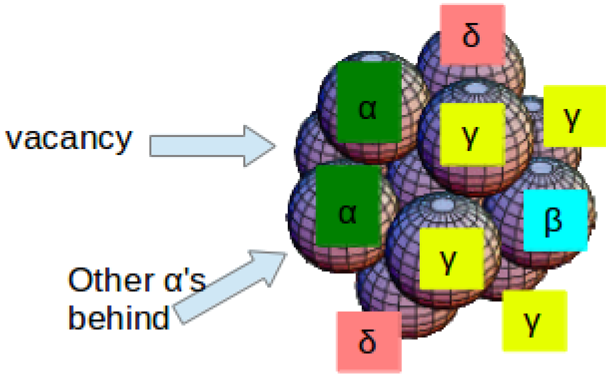

Figure 2.1: This figure illustrates the different cases of two-particle integrals for hard spheres with a vacancy as the nearest neighbor to at least one of the moving particles. The vacancy is labelled on the right, and the first moving particle is in the center of the cluster, unlabelled. The integral types for the case of each non vacant nearest neighbor site of the first moving particle being the second moving particle are denoted

As can be seen in figure 2.1, for each vacancy there are four Z_α type integrals, one Z_β, four Z_γ and two Z_δ type integrals per nearest neighbor. Therefore, since each vacancy has twelve nearest neighbors, there are twelve time each of these counts for each type for each vacancy, excepting the Z_α type integrals which are counted twice this way since each moving particle involved is a nearest neighbor of the vacancy, yielding a factor of a half in the total count of Z_α integrals. It remains for us to count the Z_{ss} type integrals. To do so, first note that for N particles and no vacancies, there are $6N$ unique nearest neighbor pairs of particles as each particle has twelve nearest neighbors, but we must divide by two as pair i, j is not distinct from pair j, i. Now if we have M sites, for each of (M-N) vacancies, twelve nearest neighbor pairs are removed. The number of remaining nearest neighbor pairs neither of which are nearest neighbors of a vacancy can then be found by subtracting the integral counts above from the total number of nearest neighbor pairs, yielding $(6N-12(M-N))-108(M-N)$ many Z_{ss} integrals.

Let us now define $\mathscr{Z}_\alpha \equiv \frac{Z_\alpha}{Z_{sv}Z_{sv}}$, $\mathscr{Z}_\beta \equiv \frac{Z_\beta}{Z_{sv}Z_s}$, $\mathscr{Z}_\gamma \equiv \frac{Z_\gamma}{Z_{sv}Z_s}$, and $\mathscr{Z}_\delta \equiv \frac{Z_\delta}{Z_{sv}Z_s}$. Assuming once more that we have M sites and N particles, we can then write the second order partition function as follows (assuming again of course that the vacancies are placed far enough apart as to be non-interacting):

$$Q_2 = Q_1 \mathscr{Z}_\alpha^{24(M-N)} \mathscr{Z}_\beta^{12(M-N)} \mathscr{Z}_\gamma^{48(M-N)} \mathscr{Z}_\delta^{24(M-N)} \left(\frac{Z_{ss}}{Z_s Z_s}\right)^{(6N-12(M-N))-108(M-N)} \tag{2.8}$$

Where Q_1 is given by equation 1.2. Note that as we know the count of each type of integral independent of configuration, the sum over l in equation 1.1 has once again reduced to a simple binomial coefficient.

The Helmholtz free energy can then easily be obtained from equation 2.8 as follows:

$$\frac{\beta F_2}{N} = -\ln(Q_2)/N \tag{2.9}$$

$$= -\frac{\ln(Q_1)}{N} - \frac{1}{N}\left((M-N)\left(24\ln(\mathscr{Z}_\alpha) + 12\ln(\mathscr{Z}_\beta) + 48\ln(\mathscr{Z}_\gamma) + 24\ln(\mathscr{Z}_\delta) - 120\ln\left(\frac{Z_{ss}}{Z_s Z_s}\right)\right) + 6N\ln\left(\frac{Z_{ss}}{Z_s Z_s}\right)\right) \tag{2.10}$$

$$= -\frac{\ln(Q_1)}{N} - \left(\frac{n_v}{1-n_v}\right)\left(24\ln(\mathscr{Z}_\alpha) + 12\ln(\mathscr{Z}_\beta) + 48\ln(\mathscr{Z}_\gamma) + 24\ln(\mathscr{Z}_\delta) - 120\ln\left(\frac{Z_{ss}}{Z_s Z_s}\right)\right) - 6\ln\left(\frac{Z_{ss}}{Z_s Z_s}\right) \tag{2.11}$$

2.3 Second Order Formation Energy for Hard Spheres

We will again determine an expression for the Gibb's free energy of monovacancy formation by minimizing the free energy with respect to the monovacancy concentration. We use the same assumption that $n_v \ll 1$, and thus ignore terms that are not logarithmic in or independent of n_v. For notational brevity, let us define the set $I = \{\alpha, \beta, \gamma, \delta\}$ and allow n_i for $i \in I$ to denote the multiplicity of integrals of type Z_i. We then proceed from the results of the section 2.2 as follows:

$$\frac{\beta\partial(F_2/N)}{\partial n_v} = \beta\frac{\partial(F_1/N)}{\partial n_v} - \frac{1}{(1-n_v)^2}\sum_{i\in I} n_i \ln(\mathscr{Z}_i) + \frac{120}{(1-n_v)^2}\ln\left(\frac{Z_{ss}}{Z_s Z_s}\right) - 6\frac{Z_s Z_s}{Z_{ss}}\left(\frac{\partial Z_{ss}}{\partial n_v}\frac{1}{Z_s^2} - 2\frac{Z_{ss}}{Z_s^3}\frac{\partial Z_s}{\partial n_v}\right) + \cdots \tag{2.12}$$

$$\approx -\frac{1}{Z_s}\frac{\partial Z_s}{\partial n_v} - 12\ln\left(\frac{Z_{sv}}{Z_s}\right) + \ln(n_v) - \sum_{i\in I} n_i \ln(\mathscr{Z}_i) + 120\ln\left(\frac{Z_{ss}}{Z_s Z_s}\right) - 6\left(\frac{1}{Z_{ss}}\frac{\partial Z_{ss}}{\partial n_v} - \frac{2}{Z_s}\frac{\partial Z_s}{\partial n_v}\right) \tag{2.13}$$

Recalling from section 1.3 that $\frac{\partial Z_s}{\partial n_v} \approx \rho Z_s'$, and noting that similarly $\frac{\partial Z_{ss}}{\partial n_v} \approx \rho Z_{ss}'$, we have that:

$$\beta\frac{\partial(F_2/N)}{\partial n_v} \approx 11\rho\frac{Z_s'}{Z_s} - 6\rho\frac{Z_{ss}'}{Z_{ss}} - 12\ln\left(\frac{Z_{sv}}{Z_s}\right) - \sum_{i\in I} n_i \ln(\mathscr{Z}_i) + 120\ln\left(\frac{Z_{ss}}{Z_s Z_s}\right) + \ln(n_v) \tag{2.14}$$

Setting this equalt zero and solving for n_v yields our new expression for $n_{v,eq}$:

$$\boxed{n_{v,eq} = \exp\left(-11\rho\frac{Z_s'}{Z_s}\right)\exp\left(6\rho\frac{Z_{ss}'}{Z_{ss}}\right)\left(\frac{Z_{sv}}{Z_s}\right)^{12}\left(\frac{Z_{ss}}{Z_s Z_s}\right)^{120}\prod_{i\in I}\mathscr{Z}_i^{n_i}} \tag{2.15}$$

For small $n_{v,eq}$, $\beta F \approx -N\ln(Z_s) - 6N\ln\left(\frac{Z_{ss}}{Z_s Z_s}\right) \Rightarrow (F/N)' \approx \beta^{-1}\left(11\frac{Z_s'}{Z_s} - 6\frac{Z_{ss}'}{Z_{ss}}\right)$. Once again using the relations $n_{v,eq} = \exp(-\beta\Delta G_v)$ and $p = (F/N)'\rho^2$, we quickly arrive at our final result:

$$\boxed{\Delta G_v = \frac{p}{\rho} - \beta^{-1}\left(12\ln\left(\frac{Z_{sv}}{Z_s}\right) - 120\ln\left(\frac{Z_{ss}}{Z_s Z_s}\right) + \sum_{i\in I} n_i \ln(\mathscr{Z}_i)\right)} \tag{2.16}$$

Like the one particle result, this expression can be decomposed into an equation of state piece (the first term), and a configuration integral piece (the second term). Note also that the second term takes the form of the one particle result for hard spheres (the leftmost term inside the parentheses) and corrections from two particle integrals (the rightmost two terms).

3 Vacancy Interaction

3.1 Helmholtz Free Energy Shift

In this section, we are interested in deriving the difference in free energy between two vacancies at some finite separation and two non-interacting vacancies. Let every particle within n_m shells of a vacancy "feel" the effect of the vacancy. Let $\sum_{i=1}^{n_m} g_i = \xi$, where g_i is the number of particles in shell i. Let the number of particles that are simultaneously within n_m shells of both vacancies, where the vacancies are separated by k shells, be denoted ξ'_k. We will denote the different kinds of integrals for particles that can feel both vacancies as $Z_{sv,ij}$ where i is the shell of the first vacancy that the particle is in, and j that of the second. In the case of interacting vacancies separated by k shells, there will be ξ'_k many more integrals of Z_s type than in the case of non-interacting vacancies, and for each $Z_{sv,ij}$, of which there are also ξ'_k many, there will be one fewer $Z_{sv,i}$ and one fewer $Z_{sv,j}$. The first equation below is then the free energy for two non-interacting vacancies. The second equation is that for two interacting vacancies. The final equation is the difference between the free energy in these two scenarios, where the outer sum is over the the possible second vacancies at a given separation (all of these terms should be the same) and the inner sum is over the particles in the overlap, of which there should be ξ'_k for vacancies at separation k. When computing this, I average by the number of particles at a given separation. I don't know if this is a good way to normalize or not.

$$\beta F = -\sum_{i=1}^{n_m} g_i \ln(Z_{sv,i}) - \sum_{j=1}^{n_m} g_j \ln(Z_{sv,j}) + \cdots \tag{3.1}$$

$$\beta F = -\sum_{i,j} \ln(Z_{sv,ij}) - \xi' \ln(Z_s) + \cdots \tag{3.2}$$

$$\Delta F = \sum\sum \ln\left(\frac{Z_{sv,ij} Z_s}{Z_{sv,i} Z_{sv,j}}\right) \tag{3.3}$$