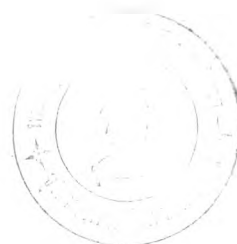


## CHAPTER III



### MATHEMATICAL DISCUSSION OF THE DIFFERENCES BETWEEN $m-P_n(c)$

#### 3.1 Cumulant Average of the Green's function<sup>21,22</sup>

If we denote " $\Delta$ " as the change in the energy when one molecule is removed to create a vacancy or one molecule is replaced by another type, the two situations are mathematically the same. However the perturbation is not just this change in energy  $\Delta$ . Because the replacement (or removal) of the molecule is occurring at random sites, the configuration averaging of these random sites will also be a perturbation. We must introduce an operator  $c$  to denote the site occupancy which have the convention that:

$$c_i = 1 ; \text{ if the B molecule (impurity) is on the site } i \text{ or} \\ \text{ if the site } i \text{ is vacant.}$$

$$c_i = 0 ; \text{ if it is not.}$$

Therefore the total Hamiltonian in the presence of impurities is

$$H' = H_0 + \Delta \sum_i c_i \quad (3.1.1)$$

The Green's function for the disordered system can be written in the form

$$\begin{aligned}
G &= \frac{1}{E-H'} \\
&= \frac{1}{E-H_0 - \Delta \sum_i c_i} \\
&= \frac{1}{E-H_0} \left( \frac{1}{1 - \frac{\Delta \sum_i c_i}{E-H_0}} \right) \quad (3.1.2)
\end{aligned}$$

Using the geometrical series expansion

$$\frac{1}{1-x} = 1 + x + x^2 + \dots + x^n + \dots \quad (3.1.3)$$

where

$$\begin{aligned}
x &= \frac{\Delta}{E-H_0} \sum_i c_i \\
x^2 &= \left( \frac{\Delta}{E-H_0} \sum_{i_1} c_{i_1} \right) \left( \frac{\Delta}{E-H_0} \sum_{i_2} c_{i_2} \right) \\
x^n &= \frac{\Delta^n}{(E-H_0)^n} \sum_{i_1, i_2, \dots, i_n} c_{i_1} c_{i_2} \dots c_{i_n} \quad (3.1.4)
\end{aligned}$$

so the Green's function can be written as (later we will use only  $c_n$  for  $c_{i_n}$  or  $i_n = n$ ,  $n = 1, 2, 3, \dots$ )

$$\begin{aligned}
G &= \frac{1}{E-H_0} \left\{ 1 + \frac{\Delta}{E-H_0} \sum c_1 + \frac{\Delta^2}{(E-H_0)^2} \sum_{1,2} c_1 c_2 \right. \\
&+ \frac{\Delta^3}{(E-H_0)^3} \sum_{1,2,3} c_1 c_2 c_3 \\
&+ \dots + \left. \frac{\Delta^n}{(E-H_0)^n} \sum_{1,2,3,\dots,n} c_1 c_2 c_3 \dots c_n + \dots \right\} \quad (3.1.5)
\end{aligned}$$

The above Green's function is for a particular crystal on which the sites occupied by the B atoms are specified. Since we need the Green's function for an average crystal, we must sum over all possible configurations. Doing this we will encounter quantities such as  $\langle c_1 c_2 \dots c_n \rangle_{\text{cum}}$  where  $\langle \rangle_{\text{cum}}$  denotes a configuration average or cumulant average. Thus the cumulant average Green's function

$$\begin{aligned} \langle G \rangle_{\text{cum}} = & \frac{1}{E - H_0} \left\{ 1 + \frac{\Delta}{E - H_0} \sum_1 \langle c_1 \rangle_{\text{cum}} \right. \\ & + \frac{\Delta^2}{(E - H_0)^2} \sum_{1,2} \langle c_1 c_2 \rangle_{\text{cum}} \\ & + \frac{\Delta^3}{(E - H_0)^3} \sum_{1,2,3} \langle c_1 c_2 c_3 \rangle_{\text{cum}} + \dots + \frac{\Delta^n}{(E - H_0)^n} \\ & \left. \sum_{1,2,\dots,n} \langle c_1 c_2 \dots c_n \rangle_{\text{cum}} + \dots \right\} \quad (3.1.6) \end{aligned}$$

### 3.2 Evaluation of $\langle c_1 c_2 \dots c_n \rangle$ in Analytical Expression<sup>21,22</sup>

The value of  $\langle c_i \rangle$  is determined from its definition

$$\begin{aligned} \langle c_i \rangle &= \text{average value of } c_i \\ &= \frac{\text{value of } c_i \text{ for each different crystal arrangement}}{\text{numbers of different crystal arrangement}} \end{aligned}$$

or

$$\langle c_i \rangle = \frac{\sum_{k=1}^N c_i^{(k)}}{N} = c \quad (3.2.1)$$

where  $c_i^{(k)}$  is the value of  $c_i$  for the  $k^{\text{th}}$  arrangement so  $c$  can be interpreted that is the concentration of impurities in disordered

system. Therefore, if we introduce  $P_n(c)$  which is the occupancy polynomial, we get

$$\begin{aligned}\langle c_1 \rangle &= c \\ &= P_1(c)\end{aligned}\quad (3.2.2a)$$

Consider for instance the configuration average of the product of two site operator  $\langle c_1 c_2 \rangle$ , we have

$$\begin{aligned}\langle c_1 c_2 \rangle &= \langle c_1 \rangle = c && \text{if } 1 = 2 ; c_1 c_2 = c_1 \\ &= \langle c_1 \rangle \langle c_2 \rangle = c^2 && \text{if } 1 \neq 2\end{aligned}$$

We will get

$$\begin{aligned}\langle c_1 c_2 \rangle &= c^2 - (c^2 - c) \delta_{12} && , \delta_{12} = 1, 1 = 2 \\ &= c^2 + (c - c^2) \delta_{12} && = 0, 1 \neq 2 \\ &= P_1^2(c) + P_2(c) \delta_{12}\end{aligned}\quad (3.2.2b)$$

Consider  $\langle c_1 c_2 c_3 \rangle$

$$\begin{aligned}\langle c_1 c_2 c_3 \rangle &= \langle c_1 \rangle = c && \text{if } 1 = 2 = 3 ; c_1 c_2 c_3 = c_1 \\ &= \langle c_1 \rangle \langle c_3 \rangle = c^2 && \text{if } 1 = 2 \neq 3 ; c_1 c_2 = c_1 \\ &= \langle c_1 \rangle \langle c_2 \rangle = c^2 && \text{if } 1 = 3 \neq 2 ; c_1 c_3 = c_1 \\ &= \langle c_1 \rangle \langle c_2 \rangle = c^2 && \text{if } 2 = 3 \neq 1 ; c_2 c_3 = c_2 \\ &= \langle c_1 \rangle \langle c_2 \rangle \langle c_3 \rangle = c^3 && \text{if } 1 \neq 2 \neq 3 ;\end{aligned}$$

We get,

$$\begin{aligned}
 \langle c_1 c_2 c_3 \rangle &= c^3 + (c^2 - c^3) (\delta_{12} + \delta_{13} + \delta_{23}) + (c - 3c^2 + 2c^3) \delta_{123} \\
 &= P_1^3(c) - P_1(c)P_2(c) (\delta_{12} + \delta_{13} + \delta_{23}) \\
 &+ P_3(c) \delta_{123} ; \quad (3.2.2c)
 \end{aligned}$$

The condition for  $\delta_{123}$  function

$$\begin{aligned}
 \delta_{123} &= 1 \quad \text{for} \quad 1 = 2 = 3 \quad ; \quad \delta_{12} = \delta_{13} = \delta_{23} = 1 \\
 &= 0 \quad \text{for} \quad 1 = 2 \neq 3 \quad \text{but} \quad \delta_{12} = 1, \quad \delta_{13} = \delta_{23} = 0 \\
 &= 0 \quad \text{for} \quad 1 = 3 \neq 2 \quad \text{but} \quad \delta_{13} = 1, \quad \delta_{12} = \delta_{23} = 0 \\
 &= 0 \quad \text{for} \quad 2 = 3 \neq 1 \quad \text{but} \quad \delta_{23} = 1, \quad \delta_{12} = \delta_{13} = 0
 \end{aligned}$$

and so forth

$$\begin{aligned}
 \langle c_1 c_2 c_3 c_4 \rangle &= P_1^4(c) + P_1^2(c) P_2(c) (\delta_{12} + \delta_{13} + \delta_{14} + \delta_{23} + \delta_{24} + \delta_{34}) \\
 &+ P_1(c) P_3(c) (\delta_{123} + \delta_{124} + \delta_{134} + \delta_{234}) \\
 &+ P_2^2(c) (\delta_{12} \delta_{34} + \delta_{13} \delta_{24} + \delta_{14} \delta_{23}) \\
 &+ P_4(c) \delta_{1234} \quad (3.2.2d)
 \end{aligned}$$

$$\begin{aligned}
 \langle c_1 c_2 c_3 c_4 c_5 \rangle &= P_1^5(c) + P_1^3(c) P_2(c) (\delta_{12} + \delta_{13} + \delta_{14} + \delta_{15} \\
 &+ \delta_{23} + \delta_{24} + \delta_{25} + \delta_{34} + \delta_{35} + \delta_{45}) \\
 &+ P_1^2(c) P_3(c) (\delta_{123} + \delta_{124} + \delta_{125} + \delta_{134} + \delta_{135} \\
 &+ \delta_{145} + \delta_{234} + \delta_{235} + \delta_{245} + \delta_{345})
 \end{aligned}$$

$$\begin{aligned}
& + P_1(c) P_2^2(c) ( \delta_{23} \delta_{45} + \delta_{24} \delta_{35} + \delta_{25} \delta_{34} \\
& + \delta_{13} \delta_{45} + \delta_{14} \delta_{35} + \delta_{15} \delta_{34} + \delta_{12} \delta_{45} + \delta_{14} \delta_{25} \\
& + \delta_{15} \delta_{24} + \dots ) \\
& + P_1(c) P_4(c) ( \delta_{2345} + \delta_{1345} + \dots ) \\
& + P_2(c) P_3(c) ( \delta_{12} \delta_{345} + \delta_{13} \delta_{245} + \dots ) \\
& + P_5(c) \delta_{12345} \tag{3.2.2e}
\end{aligned}$$

$$\begin{aligned}
\langle c_1 c_2 c_3 c_4 c_5 c_6 \rangle & = P_1^6(c) + P_1^4(c) P_2(c) ( \delta_{12} + \delta_{13} + \delta_{14} + \dots ) \\
& + P_1^3(c) P_3(c) ( \delta_{123} + \delta_{124} + \dots + \delta_{456} ) \\
& + P_1^2(c) P_2^2(c) ( \delta_{12} \delta_{34} + \delta_{12} \delta_{35} + \dots \\
& + \delta_{36} \delta_{45} ) \\
& + P_1^2(c) P_4(c) ( \delta_{1234} + \delta_{1235} + \dots + \delta_{3456} ) \\
& + P_1(c) P_2(c) P_3(c) ( \delta_{12} \delta_{345} + \delta_{13} \delta_{245} + \dots \\
& + \delta_{56} \delta_{234} ) \\
& + P_2^3(c) ( \delta_{12} \delta_{34} \delta_{56} + \delta_{12} \delta_{35} \delta_{46} + \dots \\
& + \delta_{16} \delta_{25} \delta_{34} ) \\
& + P_1(c) P_5(c) ( \delta_{12345} + \delta_{12346} + \dots + \delta_{23456} ) \\
& + P_2(c) P_4(c) ( \delta_{12} \delta_{3456} + \delta_{13} \delta_{2456} + \dots \\
& + \delta_{56} \delta_{1234} ) \\
& + P_3^2(c) ( \delta_{123} \delta_{456} + \delta_{124} \delta_{356} + \dots + \delta_{156} \delta_{234} ) \\
& + P_6(c) \delta_{123456} \tag{3.2.2f}
\end{aligned}$$

The results for  $P_n(c)$  up to  $n = 6$  are presented in Table (3.2,1)

Matsubara and Yonezawa and Maradudin had pointed out that the  $P_n(c)$  are cumulants of the indicator function for the presence of, say a B atom. So we called that  $P_n(c)$  is the cumulant coefficients of the cumulant average.

Table 3.2.1 Multiple - occupancy polynomials or cumulant coefficients  $P_n(c)$  for  $n \leq 6$ .<sup>22</sup>

$P_1(c)$	=	$c$
$P_2(c)$	=	$c - c^2$
$P_3(c)$	=	$c - 3c^2 + 2c^3$
$P_4(c)$	=	$c - 7c^2 + 12c^3 - 6c^4$
$P_5(c)$	=	$c - 15c^2 + 50c^3 - 60c^4 + 24c^5$
$P_6(c)$	=	$c - 31c^2 + 180c^3 - 390c^4 + 360c^5 - 120c^6$

### 3.3 Description of $P_n(c)$ Polynomials in Terms of Graph

In Leath and Goodman's second paper<sup>11</sup>

$$K_n^i(\mu) = \mu_B^n c(1-c)^{n-1} \quad (3.3.1)$$

is the evaluation of the 1- cumulant of Gaspard and Cyrot- Lackman.<sup>23</sup>

$K_n^i(\mu)$  is the cumulants of the random variable  $\mu$  and  $\mu_B = (M_r - M_B) \omega^2$

where  $M_r$  is the intermediate atomic mass,  $M_B$  is the atomic mass of atom type B,  $\omega$  is the frequency. For the monomer self-energy

$$\Sigma_1 = \text{---} + \text{---} + \text{---} + \text{---} + \dots$$

The approximations of  $P_n(c)$  of Hong and Kopelman, Chatuporn are

$$\text{Hong and Kopelman} \quad P_n(c) = c$$

$$\text{Chatuporn} \quad P_n(c) = \text{Stirling numbers of the second kind}$$

An inconsistency in Chatuporn's work was the calculation of  $P_n(c)$  which takes into account the exist of dimer, trimer, etc series. Leath and Goodman pointed out that the propagator in their case is based on only monomer contributions being present when calculating  $\Sigma_1$ . In determining  $\Sigma_1$  it was also assumed that the cumulants were constructed only from monomer graphs. To be self-consistent, the dimer self energy should be calculated using cumulants constructed from just monomer and dimer graphs.

We will describe the expansion of  $P_n(c)$  in terms of graph which was introduced by Aiyer, Elliott, Krumhansl and Leath<sup>24</sup> for self consistency.

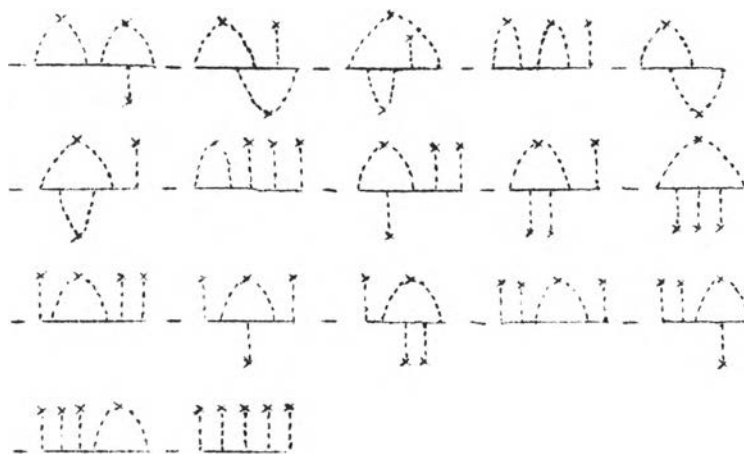
$$P_1(c) = \text{---} = c \quad (3.3.2a)$$

$$P_2(c) = \text{---} - \text{---} = c - c^2 \quad (3.3.2b)$$

$$P_3(c) = \text{---} - \text{---} - \text{---} - \text{---} - \text{---} \\ = c - 3c(c - c^2) - c^3 = c - 3c^2 + 2c^3 \quad (3.3.2c)$$

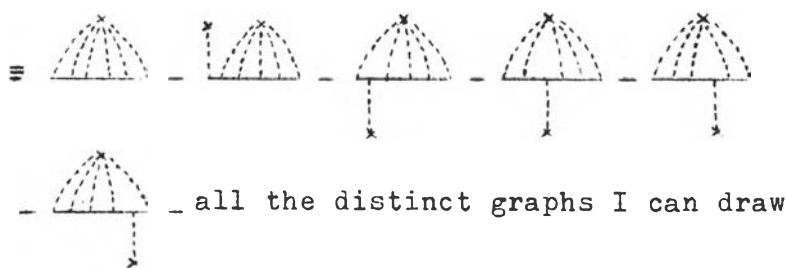






$$\begin{aligned}
 &= c - 5P_1(c)P_4(c) - 10P_2(c)P_3(c) - 10P_1^2(c)P_3(c) \\
 &\quad - 15P_1(c)P_2^2(c) - 10P_1^3(c)P_2(c) - P_1^5(c) \\
 &= c - 5c(c - 7c^2 + 12c^3 - 6c^4) - 10(c - c^2)(c - 3c^2 \\
 &\quad + 2c^3) - 10c^2(c - 3c^2 + 2c^3) - 15c(c - c^2)^2 \\
 &\quad - 10c^3(c - c^2) - c^5 \\
 &= c - 15c^2 + 50c^3 - 60c^4 + 24c^5 \tag{3.3.2c}
 \end{aligned}$$

$P_6(c)$





all the distinct graphs I can draw

Some of the distinct graphs I can draw from  $P_6(c)$



In this research we will consider only monomer and dimer graphs and so to be self consist,  $P_n(c)$  will be evaluated by considering only monomer and dimer graphs in the expansion of  $P_n(c)$

In 1 - cumulant we will get  $1 - P_n(c)$  by considering only one - complex graph  ,  , ...

$$1 - P_1(c) = c$$

$$1 - P_2(c) = c - c^2 = c(1 - c)$$



$$\begin{aligned} 1 - P_3(c) &= c - 2c(c - c^2) - c^3 = c - 2c^2 + c^3 \\ &= c(1 - c)^2 \end{aligned}$$

$$\begin{aligned} 1 - P_4(c) &= c - 2c \{1 - P_3(c)\} - \{1 - P_2(c)\}^2 \\ &\quad - 3c^2 \{1 - P_2(c)\} - c^4 \\ &= c - 3c^2 + 3c^3 - c^4 = c(1 - c)^3 \end{aligned}$$

$$\begin{aligned} 1 - P_5(c) &= c - 2c \{1 - P_4(c)\} - 2 \{1 - P_2(c)\} \\ &\quad \times \{1 - P_3(c)\} - 3c^2 \{1 - P_3(c)\} - 3c \{1 - P_2(c)\}^2 \\ &\quad - 4c^3 \{1 - P_2(c)\} - c^5 \\ &= c - 4c^2 + 6c^3 - 4c^4 + c^5 = c(1 - c)^4 \end{aligned}$$

.....

$$1 - P_n(c) = c(1 - c)^{n-1} \quad (3.3.3)$$

In 2 - cumulant we will get  $2 - P_n(c)$  by considering one - complex and two - complex graphs for example  or  and so forth are the two - complex graph. We get

$$2 - P_1(c) = c$$

$$2 - P_2(c) = c - c^2$$

$$\begin{aligned}
 2 - P_3(c) &= c - 3c^2 + 2c^3 \\
 2 - P_4(c) &= c - 7c^2 + 10c^3 - 4c^4 \\
 2 - P_5(c) &= c - 15c^2 + 32c^3 - 24c^4 + 6c^5 \quad (3.3.4)
 \end{aligned}$$

.....

which cannot be derived in the general form. The general form of  $1 - P_n(c)$  in (3.3.3) correspond to (3.3.1) which will get the monomer - self - energy in the same result obtained by Elliott and Taylor<sup>25</sup> .:

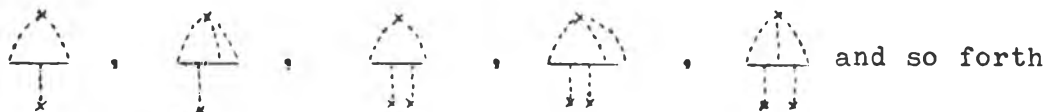
$$\Sigma_{ET}^{(1)} = \frac{\mu_B c}{1 - (1 - c)\mu_B d_0} \quad (3.3.5a)$$

our result,

$$\Sigma_1 = \frac{c \Delta}{1 - (1 - c)\Delta G_0} \quad (3.3.5b)$$

where  $\mu_B \equiv \Delta$  and  $d_0 \equiv G_0$

If in the case of 1 - cumulant , we count the one - complex term which have the other isolated scattering together such that



We will get  $P'_n(c)$  which can be derived in the general form

$$\begin{aligned}
 P'_1(c) &= c \\
 P'_2(c) &= c(1 - c) \\
 P'_3(c) &= c(1 - c)(1 - 2c) \\
 P'_4(c) &= c(1 - c)(1 - 2c)^2
 \end{aligned}$$

$$\begin{aligned}
 P'_5(c) &= c(1-c)(1-2c)^3 \\
 P'_6(c) &= c(1-c)(1-2c)^4 \\
 &\dots\dots\dots \\
 P'_n(c) &= c(1-c)(1-2c)^{n-2}, \quad n \geq 2 \quad (3.3.6)
 \end{aligned}$$

which correspond to Leath and Goodman's result :<sup>11</sup>

$$K'_n(\mu) = c(1-c)(1-2c)^{n-2} (\mu_A - \mu_B)^n \quad (3.3.7)$$

the monomer self - energy of Leath and Goodman's result is

$$\Sigma^{(1)} = \frac{(1-c)\mu_A + c\mu_B - \mu_A\mu_B d_0}{1 - \{c\mu_A + (1-c)\mu_B\} d_0} \quad (3.3.8)$$

which is formally symmetric with respect to interchange of A and B atom types.

### 3.4 Set up the Self - Energy for the Mixed Molecular Crystal

From (2.3.1) in chapter II , we have the monomer self - energy in analytical form as

$$\begin{aligned}
 \Sigma_1 &= (\Delta/N)N P_1(c) + (\Delta/N)^2 N P_2(c) \Sigma_{k'} G'_0(k) \\
 &+ (\Delta/N)^3 N P_3(c) \Sigma_{k'} \Sigma_{k''} G'_0(k) G''_0(k) + \dots
 \end{aligned} \quad (3.4.1)$$

by substituting  $P'_n(c)$  from (3.3.6) into  $P_n(c)$  we get

$$\begin{aligned}
 \Sigma_1 &= (\Delta/N)Nc + (\Delta/N)^2 Nc(1-c) \Sigma_k G'_0(k) \\
 &+ (\Delta/N)^3 Nc(1-c)(1-2c) \Sigma_k \Sigma_{k''} G'_0(k) G''_0(k'') \\
 &+ (\Delta/N)^4 Nc(1-c)(1-2c)^2 \\
 &\times \Sigma_{k'} \Sigma_{k''} \Sigma_{k'''} G'_0(k') G''_0(k'') G'''_0(k''') + \dots \\
 \Sigma_1 &= (\Delta/N)Nc + (\Delta/N)^2 N^2 c(1-c) G_0(E) \\
 &+ (\Delta/N)^3 N^3 c(1-c)(1-2c) G_0^2(E) \\
 &+ (\Delta/N)^4 N^4 c(1-c)(1-2c)^2 G_0^3(E) + \dots \\
 &= (\Delta/N)Nc \{ 1 + (\Delta/N)N(1-c) G_0(E) \\
 &+ (\Delta/N)^2 N^2(1-c)(1-2c) G_0^2(E) \\
 &+ (\Delta/N)^3 N^3(1-c)(1-2c)^2 G_0^3(E) + \dots \} \\
 \Sigma_1 &= c\Delta \left[ 1 + (\Delta/N)N(1-c) G_0(E) \right. \\
 &\times \{ 1 + (\Delta/N)N(1-2c) G_0(E) \\
 &\quad + (\Delta/N)^2 N^2(1-2c)^2 G_0^2(E) \\
 &\quad \left. + (\Delta/N)^3 N^3(1-2c)^3 G_0^3(E) + \dots \} \right] \\
 &= c\Delta \left\{ 1 + \frac{(\Delta/N)N(1-c) G_0(E)}{1 - (\Delta/N)N(1-2c) G_0(E)} \right\}
 \end{aligned}$$

$$\begin{aligned}
&= c \Delta \left\{ 1 + \frac{(1 - c) \Delta G_o(E)}{1 - (1 - 2c) \Delta G_o(E)} \right\} \\
&= c \Delta \left\{ \frac{1 - (1 - 2c) \Delta G_o(E) + (1 - c) G_o(E)}{1 - (1 - 2c) \Delta G_o(E)} \right\} \\
&= c \Delta \left\{ \frac{1 - \Delta G_o(E) + 2c \Delta G_o(E) + \Delta G_o(E) - c \Delta G_o(E)}{1 - (1 - 2c) \Delta G_o(E)} \right\} \\
&= c \Delta \left\{ \frac{1 + c \Delta G_o(E)}{1 - (1 - 2c) \Delta G_o(E)} \right\} \tag{3.4.2}
\end{aligned}$$

It can be shown that in the limit  $c \rightarrow 0$ , the above reduces to the monomer self energy obtained by Hong and Kopelman.