The Cluster Variation Method II: 2-D Grid of Zigzag Chains

Basic Theory, Analytic Solution and Free Energy Variable Distributions at Midpoint ($x_1 = x_2 = 0.5$)

Alianna J. Maren, Ph.D.

Themasis

July, 2014

First draft, 2014

THM TR2014-003(ajm)

Abstract

This *Technical Report* presents the equations for a 2-D zigzag chain of bistate units using the Cluster Variation Method (CVM), a hierarchy of approximate variational methods for representing the equilibrium state of discrete systems, and offering improvement over the classic Bethe-Peierls and mean-field approximations by using configurational variables as well as state values for determining system entropy. As with the 1-D case, an analytic solution is obtained for the case where the number of units in each state are equal (x_1=x_2=0.5). This makes it possible to express the equilibrium configuration variables in terms of the interaction enthalpy parameter h.

1 Configuration Variables in the Cluster Variation Method

The Cluster Variation Method (CVM), introduced by Kikuchi in 1951 and refined by Kikuchi and Brush in 1967, is a means of considering the entropy of a system as being more than simple distribution amongst the allowable states for individual units. Rather, it encompasses the patterns of units in space, considering nearest-neighbor, next-nearest-neighbor, and other clusters.

1.1 Relations Between Configuration Variables

We begin with a free energy equation where the entropy term represents not only the units distribution into active/inactive states, but also the ***distribution of local patterns or configurations***. We can do this; it results in a much more complex reduced equation:

$$\bar{A} = \varepsilon_1 x + \frac{\varepsilon_2}{2} x^2 + \left[\sum \alpha_i Lf x_i + \sum \beta_i Lf(y_i) + \sum \beta_i Lf(w_i) + \sum \gamma_i\, Lf(z_i)\right] = 0$$

Equation 1-1

In this equation, $Lf(v) = vln(v) - v$, where v can respectively take on the values of x_i, y_i, and w_i. Thus, for the first term within the RHS bracket of *Equation 1-1*, we have $\sum \alpha_i Lf x_i = xln(x) + (1-x)\ln(1-x)$, as the weighting coefficients α_i are each 1, and we set $x_1 = x$ and $x_2 = 1 - x$. (Note that the final terms of x – (1-x) = -1, etc., have been absorbed into $\bar{A}$.)

We give our attention now to other terms within the RHS brackets; those involving y_i and w_i. These are the nearest-neighbor and next-nearest neighbor configuration entropies, respectively. These "configuration patterns" – along with the weighting coefficients – are shown in ***Figure 1***.

Configuration (Individual)	Fraction	i (Relative preponderance)
A	x_1	1
B	x_2	1

Configuration (Nearest Neighbor)	Fraction	i (Relative preponderance)
A-A	y_1	1
A-B	y_2	2
B-B	y_3	1

Configuration (Diagonal or Next-Nearest Neighbor)	Fraction	i (Relative preponderance)
A---A	w_1	1
A---B	w_2	2
B---B	w_3	1

Configuration (Triplets)	Fraction	i (Relative preponderance)
A-A-A	z_1	1
A-A-B	z_2	2
A-B-A	z_3	1
B-A-B	z_4	1
B-B-A	z_5	2
B-B-B	z_6	1

Figure 1: Configuration variables for the Cluster Variation Method, where the first variables (individual: A, B) are the same as used in the basic Ising equation, and the remaining three (nearest neighbor, next-nearest-neighbor, and triplet) are "cluster" variables that induce pattern representations into the entropy term.

Our goal is to find equilibrium point(s) of the free energy.

In a simple Ising equation, we do this by taking the partial derivative of the free energy with respect to x, and setting it equal to zero. However, with *Equation 1-1*, we need a set of equations to express the distribution of local configurations. We use the set of partial differentials with respect to the cluster variables z_i, each of which we set to zero. We then solve the resulting set of nonlinear equations for the z_i at equilibrium as a function of the interaction energy.

1.2 Relations between Configuration Variables

In the earliest work on the Cluster Variation Method, Kikuchi[1] found the free energy for his system using an enthalpy term given as:

$$E = 2N\epsilon(-y_1 + 2y_2 - y_3).$$

Equation 1-2

The physical interpretation of *Equation 1-2* is that a nearest-neighbor interaction between two like units (y_1 and y_3) is stabilizing, or has a negative coefficient, and interactions between unlike units (y_2) is destabilizing, or positive.

For our work, we will "shift" the interaction energy base so that the interactions between like units is zero, and the interaction between unlike units (y_2), ϵ, is constant. This allows us to rephrase the enthalpy equation as:

$$E = 2N\epsilon y_2.$$

Equation 1-3

The free energy is then:

$$A = E - TS = 2N\epsilon y_2 - TS$$

Equation 1-4

To give context to the two-dimensional Cluster Variation Method (2-D CVM), composed of a rectangular grid of zigzag chains, we briefly review the one-dimensional system (1-D CVM).

We begin by considering a one-dimensional system composed of a single zigzag chain, as shown in *Figure 2*.

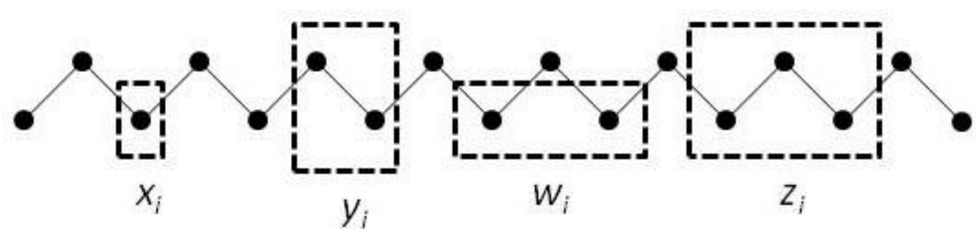

Figure 2: Single zigzag chain; the fraction variables y_i are nearest-neighbors, and the w_i are next-nearest-neighbors, which are "proximal" to their neighbors across the upper and lower portions of the chain respectively. The fraction variables z_i are comprised of any consecutive triplet.

---

[1] R. Kikuchi, *Phys. Rev.* **81**, 988 (1951), and R. Kikuchi and S.G. Brush, *J. Chem. Phys.*, **47**, 195 (1967).

A one-dimensional system (single zigzag chain) of units has the reduced Helmholtz free energy:

$$\overline{A_{1D}} = \frac{\beta A_{1D}}{N} = \beta\epsilon(z_2 + z_4 + z_3 + z_5) - 2\sum_{i=1}^{3}\beta_i\, Lf(y_i) + 2\sum_{i=1}^{6}\gamma_i Lf(z_i) + \mu\beta[1 - \sum_{i=1}^{6}\gamma_i z_i] + 4\lambda(z_3 + z_5 - z_2 - z_4),$$

Equation 1-5

where μ and λ are Lagrange multipliers.

Equation 1-5 makes use of certain relations that exist among the fraction (cluster) variables:

For the y_i:

$$y_1 = z_1 + z_2$$

$$y_2 = z_2 + z_4 = z_3 + z_5$$

$$y_3 = z_5 + z_6$$

For the w_i:

$$w_1 = z_1 + z_3$$

$$w_2 = z_2 + z_5$$

$$w_3 = z_4 + z_6$$

For the x_i:

$$x_1 = y_1 + y_2 = w_1 + w_2 = z_1 + z_2 + z_3 + z_5$$

$$x_2 = y_2 + y_3 = w_2 + w_3 = z_2 + z_4 + z_5 + z_6$$

Equation 1-6

The normalization is:

$$1 = x_1 + x_2 = \sum_{i=1}^{6}\gamma_i z_i.$$

Equation 1-7

We write the entropy of the system as the natural logarithm of the Grand Partition Function Ω:

$$S = kln\Omega,$$

Equation 1-8

where Ω, the degeneracy factor (Grand Partition Function) is the number of ways of constructing the system in such a way that the fraction variables take on certain values.

The 1-D CVM was discussed thoroughly in the preceding White Paper, *The Cluster Variation Method I: Single 1-D Zigzag Chain* (*Themasis White Paper 2014-002*).

2 The 1-D (Zigzag) Approximation in the Cluster Variation Model

2.1 CVM Entropy Using the 1-D (Zigzag) Approximation

As a review, and to provide an equation necessary for this work, we consider first the entropy of a single zigzag chain, as shown previously in *Figure 2.*

Viewing the zigzag chain as being composed of two horizontal rows, the number of ways of constructing this chain are given as:

$$\Omega_{\mathrm{double}} = \frac{\prod_{i=1}^{3}\left(2M_{y_i}\right)!^{\beta_i}}{\prod_{i=1}^{3}\left(2M_{z_i}\right)!^{\gamma_i}}$$

Equation 2-1

where M is the number of lattice points in a row, and Ω_{double} refers to the juxtaposition of two rows[2].

When M is large, Stirling's approximation[3] can be used to express *Equation 2-1* as:

$$\Omega_{\mathrm{double}} = \left[\frac{\prod_{i=1}^{3}\left(M_{y_i}\right)!^{\beta_i}}{\prod_{i=1}^{3}\left(M_{z_i}\right)!^{\gamma_i}}\right]^2$$

Equation 2-2

We substitute from *Equation 2-2* to *Equation 2-1* and once again use Stirling's approximation to obtain:

$$S_{1-D} = kln\Omega_{double} = 2k\left[\sum_{i=1}^{3}\beta_i Lf(y_i) - \sum_{i=1}^{6}\gamma_i Lf(z_i)\right],$$

Equation 2-3

where $Lf(x) = xln(x) - x$.

This is the entropy associated with a single zigzag chain.

[2] S. Miyatami, *J. Phys. Soc., Japan*, **34**, 423 (1974).

[3] Stirling's approximation is given as: *N! = N ln(N) - N*

2.2 CVM Entropy Using the 2-D (Zigzag) Approximation

We now consider the case of a two-dimensional system composed of layered zigzag chains, as illustrated in the following *Figure 3*.

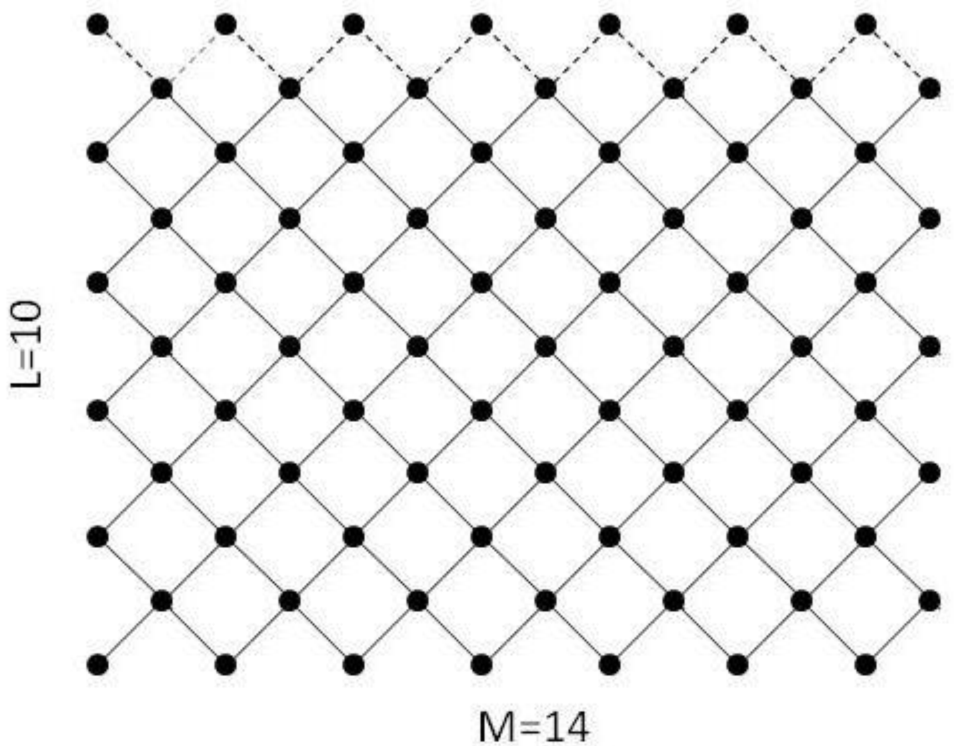

Figure 3: 2-D CVM system composed of layered zigzag chains, where in this instance, the number of elements in a single zigzag chain, M, is 14, and the number of chains, L, is 10.

The total number of ways to add the L+1th row to an existing LxM grid is the ratio of $\Omega_{double}/\Omega_{single}$, where Ω_{single} is the number of ways of constructing a single row:

$$\Omega_{single} = \frac{\prod_{i=1}^{2}(Mx_i)!}{\prod_{i=1}^{3}(Mw_i)!^{\beta_i}}$$

Equation 2-4

The number of ways of adding L rows and completing the entire system are

$$\Omega = \left[\Omega_{double}/\Omega_{single}\right]^L = \left[\frac{\prod_{i=1}^{3}(My_i)!^{2\beta_i}\prod_{i=1}^{3}(Mw_i)!^{\beta_i}}{\prod_{i=1}^{2}(Mx_i)!\prod_{i=1}^{6}(Mz_i)!^{2\gamma_i}}\right]^L$$

Equation 2-5

Since we have

$$S = kln\Omega$$

Equation 2-6

Where Ω is the degeneracy factor, as just given, we can substitute from *Equation 2-5* into *Equation 2-6* to obtain

$$S = kln\left[\frac{\prod_{i=1}^{3}(My_i)!^{2\beta_i}\prod_{i=1}^{3}(Mw_i)!^{\beta_i}}{\prod_{i=1}^{2}(Mx_i)!\prod_{i=1}^{6}(Mz_i)!^{2\gamma_i}}\right]^L$$

$$= kL\left[\sum_{i=1}^{3} 2\beta_i ln\big((My_i)!\big) + \sum_{i=1}^{3} \beta_i ln\big((Mw_i)!\big) - \sum_{i=1}^{2} ln\big((Mx_i)!\big) - \sum_{i=1}^{6} 2\gamma_i ln\big((Mz_i)!\big)\right]$$

Equation 2-7

It can be shown that

$$ln\big((Mx)!\big) = M[xlnx - x]$$

Equation 2-8

and in this work we let

$$Lf(x) = xln(x) - x$$

Equation 2-9

Substituting, we obtain

$$S = kln\Omega = \mathrm{kLM}\left[\sum_{i=1}^{3} 2\beta_i Lf(y_i) + \sum_{i=1}^{3} \beta_i Lf(w_i) - \sum_{i=1}^{2} Lf(x_i) - \sum_{i=1}^{6} 2\gamma_i Lf(z_i)\right]$$

Equation 2-10

2.3 Free Energy for the 2-D System

We refer now to the free energy equation

$$G_{2-D} = ML\epsilon(2y_2) - TS$$

Equation 2-11

Multiply through by $\beta/N = \beta/ML$, where $\beta = 1/kT$, to obtain

$$\frac{\beta}{N}G_{2-D} = \beta\epsilon(2y_2) - \left[\sum_{i=1}^{3} 2\beta_i Lf(y_i) + \sum_{i=1}^{3} \beta_i Lf(w_i) - \sum_{i=1}^{2} Lf(x_i) - \sum_{i=1}^{6} 2\gamma_i Lf(z_i)\right] + \mu\beta\left(1 - \sum_{i=1}^{6}\gamma_i z_i\right) + 4\lambda(z_3 + z_5 - z_2 - z_4)$$

Equation 2-12

where the last two terms are Lagrangian factors, as was done previously for the 1-D case.

Drawing on the relationship for y_2 given in *Equation 1-6*, we have

$$2y_2 = z_2 + z_4 + z_3 + z_5$$

Equation 2-13

Substituting from *Equation 2-13* into *Equation 2-12,* we have

$$\frac{\beta}{N}G_{2-D} = \beta\epsilon(z_2 + z_4 + z_3 + z_5) - \left[\sum_{i=1}^{3} 2\beta_i Lf(y_i) + \sum_{i=1}^{3} \beta_i Lf(w_i) - \sum_{i=1}^{2} Lf(x_i) - \sum_{i=1}^{6} 2\gamma_i Lf(z_i)\right] + \mu\beta\left(1 - \sum_{i=1}^{6}\gamma_i z_i\right) + 4\lambda(z_3 + z_5 - z_2 - z_4)$$

Equation 2-14

We recall, in comparison, that the 1-D equation (given in the preceding White Paper) was

$$\frac{\beta G_{1-D}}{M} = \beta\epsilon(z_2 + z_3 + z_4 + z_5) - 2\sum_{i=1}^{3}\beta_i Lf(y_i) + 2\sum_{i=1}^{6}\gamma_i Lf(z_i) + \mu\beta\left(1 - \sum_{i}\gamma_i z_i\right) + 4\lambda(z_3 + z_5 - z_2 - z_4)$$

Equation 2-15

where as before, μ and λ are Lagrange multipliers.

We note that the difference in the two free energy formulations is that the 2-D case includes entropy terms involving w_i and x_i.

2.4 Free Energy Minimization in the 2-D System

Taking the derivative of G_{2-D} with respect to the six configuration variables z_i, and setting each derivative equal to zero yields the following six equations, presented in detail in Appendix A:

$$z_1 q = y_1 \left(\frac{w_1}{x_1}\right)^{1/2}$$

$$z_2 q = (y_1 y_2 w_2)^{1/2} (x_1 x_2)^{-1/4} e^{-\beta\epsilon/4} e^{\lambda}$$

$$z_3 q = y_2 \left(\frac{w_1}{x_1}\right)^{1/2} e^{-\beta\epsilon/2} e^{-2\lambda}$$

$$z_4 q = y_2 \left(\frac{w_3}{x_2}\right)^{1/2} e^{-\beta\epsilon/2} e^{2\lambda}$$

$$z_5 q = (y_2 y_3 w_2)^{1/2} (x_1 x_2)^{-1/4} e^{-\beta\epsilon/4} e^{-\lambda}$$

$$z_6 q = y_3 \left(\frac{w_3}{x_2}\right)^{1/2}$$

Equation 2-16

where $q = e^{-\mu\beta/2}$, and μ can be shown to be (for chemical systems) the chemical potential.

The following *Table 1* compares the cluster variable fraction expressions for the 1-D and 2-D cases at equilibrium.

Cluster Variable z_i	**1-D Expression**	**2-D Expression**
$\boldsymbol{z_1 q}$	y_1	$y_1 \left(\frac{w_1}{x_1}\right)^{1/2}$
$\boldsymbol{z_2 q}$	$(y_1 y_2)^{1/2} e^{-\beta\epsilon/4} e^{\lambda}$	$(y_1 y_2 w_2)^{1/2} (x_1 x_2)^{-1/4} e^{-\beta\epsilon/4} e^{\lambda}$
$\boldsymbol{z_3 q}$	$y_2 e^{-\beta\epsilon/2} e^{-2\lambda}$	$y_2 \left(\frac{w_1}{x_1}\right)^{1/2} e^{-\beta\epsilon/2} e^{-2\lambda}$
$\boldsymbol{z_4 q}$	$y_2 e^{-\beta\epsilon/2} e^{2\lambda}$	$y_2 \left(\frac{w_3}{x_2}\right)^{1/2} e^{-\beta\epsilon/2} e^{2\lambda}$
$\boldsymbol{z_5 q}$	$(y_2 y_3)^{1/2} e^{-\beta\epsilon/4} e^{-\lambda}$	$(y_2 y_3 w_2)^{1/2} (x_1 x_2)^{-1/4} e^{-\beta\epsilon/4} e^{-\lambda}$
$\boldsymbol{z_6 q}$	y_3	$y_3 \left(\frac{w_3}{x_2}\right)^{1/2}$

Table 1: Expressions for the equilibrium values for the fraction variables z_i, for the 1-D and 2-D cases

For the system where $x_1 = x_1 = 0.5$ and $\lambda = 0$, *Equation 2-16* can be solved for the fraction variables y_i and z_i. The calculations, briefly summarized in the following paragraphs, are presented in more detail in *Appendix B.*

Let $h = e^{\beta\epsilon/4}$, and $s = z_1/z_3$. Then

$$z_3 = \frac{(h^2-3)(h^2+1)}{8[h^4-6h^2+1]}$$

Equation 2-17

and

$$z_1 = sz_3$$

Equation 2-18

and

$$z_2 = [1-2z_1-2z_3]/4$$

Equation 2-19

and

$$y_2 = [1-2z_1+2z_3]/4$$

Equation 2-20

We have an analytic solution for the full set of fraction variables only at $x_1 = x_2 = 0.5$, which is

$$z_1 = z_6$$

$$z_2 = z_6$$

$$z_3 = z_4$$

$$w_1 = w_3$$

$$y_1 = y_3$$

$$y_3 = 0.5 - y_2$$

$$w_3 = 0.5 - w_2$$

Equation 2-21

and the remaining fraction variables are readily obtained.

3 Analytic Solution for $x_1 = x_2 = 0.5$

When allowed to stabilize, the system comes to equilibrium at free energy minima, where the free energy equation involves both an interaction energy between terms and also an entropy term that includes the cluster variables. This computation addresses a system composed of a rectangular grid of zigzag chains.

I have computed an analytic solution for representing one of the cluster variables, *z3*, as a function of the reduced interaction energy term: $h = e^{\beta\epsilon/4}$. From this, the remaining cluster variables are found as functions of *h*.

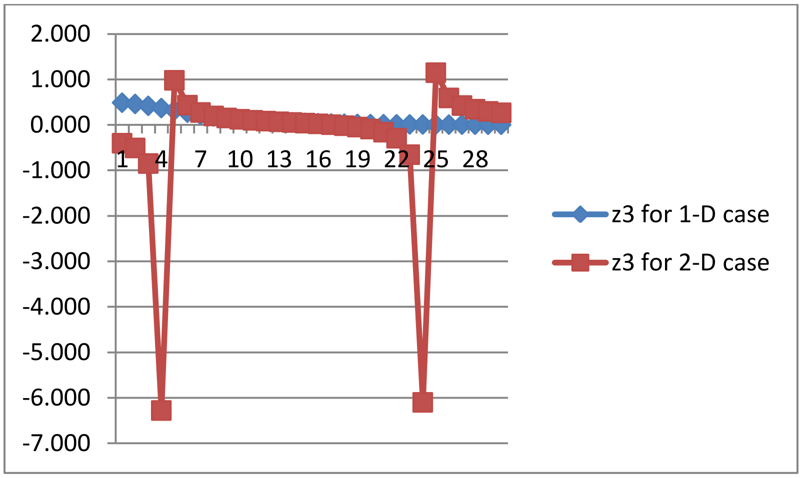

Figure 4: Results for the configuration variable z3 for both the 1-D and 2-D cases. Values for h*10 are plotted along the x-axis. The 2-D case has discontinuities, due to the quadratic nature of the denominator.

The point on this graph where *h=1* (the x-axis is 10) corresponds to $h = e^{\beta\epsilon/4}$. Effectively, *beta*epsilon* => 0. This is the case where either the interaction energy (*epsilon*) is very small, or the temperature is very large. Either way, we would expect – at this point – the most "disordered" state. The cluster variables should all achieve their nominal distributions; *z1*=*z3*=0.125, and *y2*=0.25. This is precisely what we observe.

The 2-D values for z_3 are close to those for the 1-D case in the neighborhood of *h=1*, as is shown in the following more detailed figure.

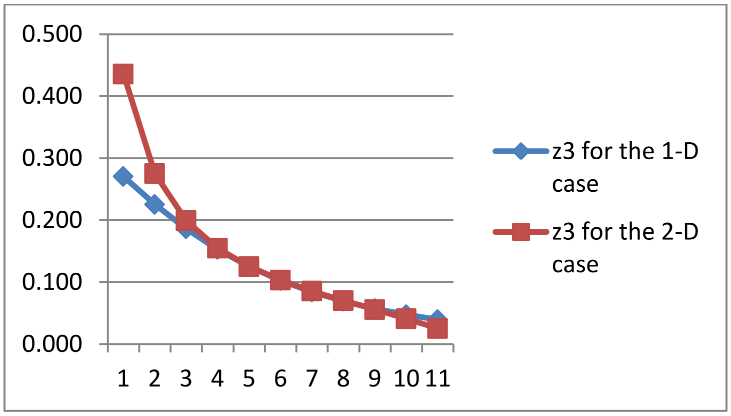

Figure 5. *h* ranges from 0.6 (LHS) to 1.6 (RHS). The new x-coordinate = 10(h)-5. When h=1, the x-coord in this figure is 5. Both values for z3 are the expected 0.125.

Consider the case of positive interaction energy between unlike units (the A-B pairwise combination). The positive interaction energy (ϵ>0) then suggests that a preponderance of A-B pairs (*y2*) would destabilize the system. We would expect that as ϵ increases as a positive value, that we would minimize *y2*, and also see small values for those triplets that involve non-similar pair combinations. That is, the A-B-A triplet, or z_3, approaches zero (and actually goes negative). We observe this on the RHS of *Figure 5*. This is the case where as $h = e^{\beta\epsilon/4}$ moves into the positive range (0-2), we see that z_3 falls towards zero.

This is the realm of creating a highly structured system where large "domains" of like units mass together. These large domains (comprised of overlapping A-A-A and B-B-B triplets) stagger against each other, with relatively few instances of "islands" (e.g., the A-B-A and B-A-B triplets.)

Naturally, this approach – using a "reduced energy term" of $\beta\epsilon$, where $\beta = 1/(kT)$, does not tell us whether we are simply increasing the interaction energy or reducing the temperature; they amount to the same thing. Both give the same resulting value for h, and it is the effect of h that we are interested in when we map the CVM variables and (ultimately) the CVM phase space.

At the LHS of the preceding graph, we have the case where $h = e^{\beta\epsilon/4}$ is small (0.5 – 1). These small values mean that we are taking the exponent of a negative number; the interaction energy between two unlike units (A-B) is negative. This means that we stabilize the system through providing a different kind of structure; one which emphasizes alternate units, e.g. A-B-A-B …

This is precisely what we observe. The cluster variable z_3 increases substantially, indicating that the configurations are largely of unlike units (A-B-A), meaning that there is very little clustering of like units into domains.

4 Discussion

The Cluster Variation Method is gaining importance in graph theory, and as a means of computing stable states in belief propagation networks. See extensive discussions by Pelizzola and by Yedidia, Freeman, and Weiss, cited in the Research Bibliography.

5 Research Bibliography

Kikuchi, R., *Phys. Rev.* **81**, 988 (1951).

Kikuchi, R., and Brush, S.G., *J. Chem. Phys.*, **47**, 195 (1967).

Maren, A.J. (2014). *The Cluster Variation Method I: 1-D Single Zigzag Chain: Basic Theory, Analytic Solution and Free Energy Variable Distributions at Midpoint (x1=x2=0.5)*, Themasis Technical Report *THM TR2014-002 (ajm).*

Maren, A.J. (2014). *Statistical Thermodynamics: Introduction to Phase Space and Metastable States*. Themasis Technical Report *THM TR2014-001 (ajm).*

Maren, A.J. (2013). *Statistical Thermodynamics: Basic Theory and Equations*. Themasis Technical Report *THM TR2013-001 (ajm).*

Maren, A.J. (2008). *Analytic Single-Point Solution for the Cluster Variation Method Variables at $x_1=x_2=0.5$*, Blogpost in www.aliannajmaren.com, accessed March 12, 2014. See http://www.aliannajmaren.com/2011/12/08/analytic-single-point-solution-for-cluster-variation-method-variables-at-x1x20-5/.

Maren, A.J. (1981). *Theoretical Models for Solid State Phase Transitions*, Ph.D. Dissertation, Arizona State University.

Miyatami, S. *J. Phys. Soc., Japan*, **34**, 423 (1974).

Pelizzola, A. (preprint, 2007). Cluster Variation Method in statistical physics and probabilistic graph models, *J. Phys. A: Math. Gen.* (submitted)

Schwartz, E., & Maren, A.J. (1994). Domains of interacting neurons: A statistical mechanical model, in *Proc. World Congress on Neural Networks (WCNN).*

Yedidia, J.S., Freeman, W.T., & Weiss, Y. (2002, January). Understanding belief propagation and its generalizations. *Mitsubishi Electric Research Laboratories MERL TR-2001-22* (www.merl.com)

APPENDIX A: 1-D ZIGZAG CHAIN – PRELIMINARY CONFIGURATION VARIABLE EQUATIONS (X_1=X_2=0.5)

This Appendix presents the details of the results given in Section 2, recapitulated as

$$z_1 q = y_1 \left(\frac{w_1}{x_1}\right)^{1/2}$$

$$z_2 q = (y_1 y_2 w_2)^{1/2} (x_1 x_2)^{-1/4} e^{-\beta\epsilon/4} e^{\lambda}$$

$$z_3 q = y_2 \left(\frac{w_1}{x_1}\right)^{1/2} e^{-\beta\epsilon/2} e^{-2\lambda}$$

$$z_4 q = y_2 \left(\frac{w_3}{x_2}\right)^{1/2} e^{-\beta\epsilon/2} e^{2\lambda}$$

$$z_5 q = (y_2 y_3 w_2)^{1/2} (x_1 x_2)^{-1/4} e^{-\beta\epsilon/4} e^{-\lambda}$$

$$z_6 q = y_3 \left(\frac{w_3}{x_2}\right)^{1/2}$$

Replicate Equation 2-16 (from main body of text)

We find these relationships by differentiating the free energy expression $G_{2\text{-}D}$ with respect to each of the cluster variables and setting the result to zero.

We begin with the free energy expression for the 2-D Cluster Variation Method (CVM), where the enthalpy is defined as an interaction energy only between unlike units, that is, $H=f(y_2)$.

For a two-dimensional system (set of overlayered zigzag chains), the free energy is

$$\begin{aligned}\frac{\beta}{N} G_{2-D} = \beta\epsilon(z_2 + z_4 + z_3 + z_5 2y_2) \\ - \left[\sum_{i=1}^{3} 2\beta_i Lf(y_i) + \sum_{i=1}^{3} \beta_i Lf(w_i) - \sum_{i=1}^{2} Lf(x_i) - \sum_{i=1}^{6} 2\gamma_i Lf(z_i)\right] \\ + \mu\beta\left(1 - \sum_{i=1}^{6} \gamma_i z_i\right) + 4\lambda(z_3 + z_5 - z_2 - z_4)\end{aligned}$$

Replicate Equation 2-14 (from main body of text)

where μ and λ are Lagrange multipliers.

We now find the expressions for each of the cluster variables z_i.

Our first step is to find the dependence of $G_{2\text{-}D}$ on z_1.

$$0 \equiv \frac{\partial G_{2-D}}{\partial z_1} = \frac{\partial}{\partial z_1}\left[\sum_{i=1}^{3} 2\beta_i Lf(y_i) + \sum_{i=1}^{3} \beta_i Lf(w_i) - \sum_{i=1}^{2} Lf(x_i) - \sum_{i=1}^{6} 2\gamma_i Lf(z_i)\right] - \mu\beta$$

Appendix A: Equation 1

We use the following relationship, originally established in *The Cluster Variation Method I: 1-D Single Zigzag Chain: Basic Theory, Analytic Solution and Free Energy Variable Distributions at Midpoint (x1=x2=0.5), THM TR2014-002 (ajm)*:

$$\frac{\partial Lf(y)}{\partial x} = \frac{\partial}{\partial x}[yln(y) - \ y] = \left[\ln(y) + \ y\ \left(\frac{1}{y}\right) - 1\right]\frac{\partial y}{\partial x}$$

or

$$\frac{\partial Lf(y)}{\partial x} = \ln\,(y)\frac{\partial y}{\partial x}$$

Appendix A: Equation 2

We use the equivalence relations introduced in Section 1.2 for the y_i:

$$y_1 = z_1 + z_2$$

$$y_2 = z_2 + z_4 = z_3 + z_5$$

$$y_3 = z_5 + z_6$$

For the w_i:

$$w_1 = z_1 + z_3$$

$$w_2 = z_2 + z_5$$

$$w_3 = z_4 + z_6$$

For the x_i:

$$x_1 = y_1 + y_2 = w_1 + w_2 = z_1 + z_2 + z_3 + z_5$$

$$x_2 = y_2 + y_3 = w_2 + w_3 = z_2 + z_4 + z_5 + z_6$$

Replicate portion of Equation 1-6

The only dependency from the y_i on z_1 is with y_1. Likewise, the only dependency from the w_i on z_1 is with w_1. Thus, recalling that the degeneracy factors $\beta_1 = \gamma_1 = 1$, we have

$$0 \equiv \frac{\partial G_{2-D}}{\partial z_1} = -2\frac{\partial}{\partial z_1}Lf(y_1) - \frac{\partial}{\partial z_1}Lf(w_1) + \frac{\partial}{\partial z_1}Lf(x_1) + 2\frac{\partial}{\partial z_1}Lf(z_1) - \mu\beta$$

or

$$0 \equiv \frac{\partial G_{2-D}}{\partial z_1} = -2ln(y_1)\frac{\partial y_1}{\partial z_1} - ln(w_1)\frac{\partial w_1}{\partial z_1} + ln(x_1)\frac{\partial x_1}{\partial z_1} + 2ln(z_1)\frac{\partial z_1}{\partial z_1} - \mu\beta$$

or

$$0 \equiv \frac{\partial G_{2-D}}{\partial z_1} = -2ln(y_1) - ln(w_1) + ln(x_1) + 2ln(z_1) - \mu\beta$$

Appendix A: Equation 3

Thus we have

$$2ln(z_1) - \mu\beta = 2ln(y_1) + ln(w_1) - ln(x_1)$$

Appendix A: Equation 4

Taking the exponent of both sides, we have

$${z_1}^2 \exp(-\mu\beta) = {y_1}^2 \frac{w_1}{x_1}$$

Appendix A: Equation 5

Or, setting $q = \exp\left(\frac{-\mu\beta}{2}\right)$, we have

$$z_1 \mathrm{q} = y_1 \left[\frac{w_1}{x_1}\right]^{1/2}$$

Appendix A: Equation 6

Now, we compute the dependence of $G_{2\text{-}D}$ on z_2.

We recall that the degeneracy factors are $\beta_1 = \gamma_1 = 1$ and $\beta_2 = \gamma_2 = 2$, so that we have

$$\begin{aligned} 0 \equiv \frac{\partial G_{2-D}}{\partial z_2} & \\ &= \frac{\partial \beta\epsilon}{\partial z_2}[z_2 + z_4 + z_3 + z_5] \\ &- \frac{\partial}{\partial z_2}\left[2\sum_{i=1}^{3}\beta_i\, Lf(y_i) + \sum_{i=1}^{3}\beta_i Lf(w_i) - \sum_{i=1}^{2} Lf(x_i) - 2\sum_{i=1}^{3}\gamma_i\, Lf(z_i)\right] \\ &- \mu\beta\frac{\partial[\gamma_2 z_2]}{\partial z_2} + 4\lambda\frac{\partial[-z_2]}{\partial z_2} \end{aligned}$$

Appendix A: Equation 7

Simplifying, we have

$$0 = \beta\epsilon - \frac{2\partial}{\partial z_2}[Lf(y_1) + 2Lf(y_2)] - \frac{\partial}{\partial z_2}[2Lf(w_2)] + \frac{\partial}{\partial z_2}[Lf(x_1) + Lf(x_2)] + \frac{2\partial}{\partial z_2}[2Lf(z_2)] - 2\mu\beta - 4\lambda$$

Appendix A: Equation 8

In particular, both here and throughout all this work, we use the following relationship:

$$2y_2 = z_2 + z_4 + z_3 + z_5$$

Appendix A: Equation 9

Thus, we find that

$$\frac{2\partial}{\partial z_2}[2Lf(y_2)] = 2\ln(y_2)\frac{\partial}{\partial z_2}[2(y_2)] = \ln(y_2)\frac{\partial}{\partial z_2}[z_2 + z_4 + z_3 + z_5] = \ln(y_2)$$

Appendix A: Equation 10

We substitute this into *Appendix A: Equation 8* to obtain

$$0 = \beta\epsilon - 2\ln(y_1) - 2\ln(y_2) - 2\ln(w_2) + \ln(x_1) + \ln(x_2) + 4\ln(z_2) - 2\mu\beta - 4\lambda$$

or

$$0 = \frac{\beta\epsilon}{2} - \ln(y_1) - \ln(y_2) - \ln(w_2) + \frac{1}{2}\ln(x_1) + \frac{1}{2}\ln(x_2) + 2\ln(z_2) - \mu\beta - 2\lambda$$

Appendix A: Equation 11

Rearranging terms, we have

$$2\ln(z_2) - \mu\beta = \ln(y_1) + \ln(y_2) + \ln(w_2) - \frac{1}{2}\ln(x_1) - \frac{1}{2}\ln(x_2) - \frac{\beta\epsilon}{2} + 2\lambda$$

Appendix A: Equation 12

We take the exponent of both sides to obtain

$${z_2}^2 \exp(-\mu\beta) = y_1 y_2 w_2 [x_1 x_2]^{-1/2} exp\left(-\frac{\beta\epsilon}{2}\right)\ exp(2\lambda)$$

Appendix A: Equation 13

We take the square root of both sides to obtain

$$z_2 \exp\left(-\frac{\mu\beta}{2}\right) = (y_1 y_2 w_2)^{1/2}[x_1 x_2]^{-1/4} exp\left(-\frac{\beta\epsilon}{4}\right)\ exp(\lambda)$$

Appendix A: Equation 14

As before, we let $q = \exp\left(\frac{-\mu\beta}{2}\right)$, to obtain

$$z_2 \mathrm{q} = (y_1 y_2 w_2)^{1/2}(y_1 y_2 w_2)^{1/2}[x_1 x_2]^{-1/4} exp\left(-\frac{\beta\epsilon}{4}\right)\ exp(\lambda)$$

Appendix A: Equation 15

Our third step in this Appendix is to compute the dependence of $G_{2\text{-}D}$ on z_3.

We recall that the degeneracy factors are $\beta_1 = \beta_3 = \gamma_1 = \gamma_3 = 1$ and $\beta_2 = \gamma_2 = 2$, so that we have

$$\begin{aligned}
0 \equiv \frac{\partial G_{2-D}}{\partial z_3} \\
&= \frac{\partial \beta\epsilon}{\partial z_3}[z_2 + z_4 + z_3 + z_5] \\
&+ \frac{-\partial}{\partial z_3}\left[2\sum_{i=1}^{3}\beta_i\, Lf(y_i) + \sum_{i=1}^{3}\beta_i Lf(w_i) - \sum_{i=1}^{2} Lf(x_i) - 2\sum_{i=1}^{3}\gamma_i\, Lf(z_i)\right] \\
&- \mu\beta\frac{\partial[\gamma_3 z_3]}{\partial z_3} + 4\lambda\frac{\partial[z_3]}{\partial z_3}
\end{aligned}$$

Appendix A: Equation 16

Doing the most obvious simplifications, we have

$$\begin{aligned}
0 = \beta\epsilon + \frac{\partial}{\partial z_3}\left[-2\sum_{i=1}^{3}\beta_i\, Lf(y_i) - \sum_{i=1}^{3}\beta_i Lf(w_i) + \sum_{i=1}^{2} Lf(x_i) + 2\sum_{i=1}^{3}\gamma_i\, Lf(z_i)\right] - \mu\beta \\
+ 4\lambda
\end{aligned}$$

Appendix A: Equation 17

From Eqn. 2-6, we recognize that the only dependence of the y_i on z_3 is with y_2. Further, the only dependence of the w_i on z_3 is with w_1, and the only dependence of the x_i on z_3 is with x_1. Also, we had previously identified that $2y_2 = z_2 + z_4 + z_3 + z_5$ (*Appendix A: Equation 9*).

This gives us

$$0 = \beta\epsilon - \frac{2\partial}{\partial z_3}[2Lf(y_2)] - \frac{\partial}{\partial z_3}[Lf(w_1)] + \frac{\partial}{\partial z_3}[Lf(x_1)] + \frac{2\partial}{\partial z_3}[Lf(z_3)] - \mu\beta + 4\lambda$$

or

$$0 = \beta\epsilon - 2ln(y_2)\frac{\partial}{\partial z_3}[2(y_2)] - \ ln(w_1)\frac{\partial w_1}{\partial z_3} + ln(x_1)\frac{\partial x_1}{\partial z_3} + 2\ ln(z_3) - \mu\beta + 4\lambda$$

or

$$0 = \beta\epsilon - 2ln(y_2) - \ ln(w_1) + ln(x_1) + 2\ ln(z_3) - \mu\beta + 4\lambda$$

or

$$0 = \frac{\beta\epsilon}{2} - ln(y_2) - \frac{1}{2}ln(w_1) + \frac{1}{2}ln(x_1) + \ ln(z_3) - \frac{\mu\beta}{2} + 2\lambda$$

Appendix A: Equation 18

We can reorganize this as

$$ln(z_3) - \frac{\mu\beta}{2} = ln(y_2) + \ \frac{1}{2}ln(w_1) - \frac{1}{2}ln(x_1) - \frac{\beta\epsilon}{2} - 2\lambda$$

Appendix A: Equation 19

We take the exponent of both sides to obtain

$$z_3 \exp\left(-\frac{\mu\beta}{2}\right) = y_2\left[\frac{w_1}{x_1}\right]^{1/2} exp\left(-\frac{\beta\epsilon}{2}\right)\ exp(-2\lambda)$$

or

$$z_3\mathrm{q} = y_2\left[\frac{w_1}{x_1}\right]^{1/2} exp\left(-\frac{\beta\epsilon}{2}\right)\ exp(-2\lambda)$$

Appendix A: Equation 20

Computations for the configuration variables z_4, z_5, and z_6 are similar to those just done, yielding the final set of equations given as *Equation 2-16*.

APPENDIX B: 1-D ZIGZAG CHAIN ANALYTIC SOLUTION (x_1=x_2=0.5)

This Appendix takes the results given in Section 2, recapitulated below, to find the definitions for the cluster variables in terms of the energy interaction parameter $h = e^{\beta\epsilon/4}$. We begin with the results found in *Appendix A*:

$$z_1 q = y_1 \left(\frac{w_1}{x_1}\right)^{1/2}$$

$$z_2 q = (y_1 y_2 w_2)^{1/2}(x_1 x_2)^{-1/4} e^{-\beta\epsilon/4} e^{\lambda}$$

$$z_3 q = y_2 \left(\frac{w_1}{x_1}\right)^{1/2} e^{-\beta\epsilon/2} e^{-2\lambda}$$

$$z_4 q = y_2 \left(\frac{w_3}{x_2}\right)^{1/2} e^{-\beta\epsilon/2} e^{2\lambda}$$

$$z_5 q = (y_2 y_3 w_2)^{1/2}(x_1 x_2)^{-1/4} e^{-\beta\epsilon/4} e^{-\lambda}$$

$$z_6 q = y_3 \left(\frac{w_3}{x_2}\right)^{1/2}$$

Replicate Equation 2-16 (from main body of text)

Let $h = e^{\beta\epsilon/4}$, and $\lambda = 0$. Then

$$z_1 q = y_1 \left(\frac{w_1}{x_1}\right)^{1/2}$$

$$z_2 q = (y_1 y_2 w_2)^{1/2}(x_1 x_2)^{-1/4} h^{-1}$$

$$z_3 q = y_2 \left(\frac{w_1}{x_1}\right)^{1/2} h^{-2}$$

$$z_4 q = y_2 \left(\frac{w_3}{x_2}\right)^{1/2} h^{-2}$$

$$z_5 q = (y_2 y_3 w_2)^{1/2}(x_1 x_2)^{-1/4} h^{-1}$$

$$z_6 q = y_3 \left(\frac{w_3}{x_2}\right)^{1/2}$$

Appendix B: Equation 1

We take the equilibrium case where $x_1 = x_2 = 0.5$ to give us

$$z_1 q = y_1 (w_1)^{1/2} 2^{1/2}$$

$$z_2 q = (y_1 y_2 w_2)^{1/2} 2^{1/2} h^{-1}$$

$$z_3 q = y_2 (w_1)^{1/2} 2^{1/2} h^{-2}$$

$$z_4 q = y_2 (w_3)^{1/2} 2^{1/2} h^{-2}$$

$$z_5 q = (y_2 y_3 w_2)^{1/2} 2^{1/2} h^{-1}$$

$$z_6 q = y_3 (w_3)^{1/2} 2^{1/2}$$

Appendix B: Equation 2

Since $y_1 = y_3$ at $x_1 = x_2$, it follows that when at $x_1 = x_2$, we also have

$$z_1 = z_6$$

$$z_2 = z_5$$

$$z_3 = z_4$$

Appendix B: Equation 3

Thus, we need only address the first three equations within the set *Appendix B: Equation 2*.

Since the factor of $2^{1/2}$ appears in all of these equations, we redefine q to include this term so that

$$q_{new} = 2^{-1/2} q_{old} = 2^{-1/2} \exp\left(\frac{-\mu\beta}{2}\right)$$

Appendix B: Equation 4

We now focus our attention on the set of three equations

$$z_1 q = y_1 (w_1)^{1/2}$$

$$z_2 q = (y_1 y_2 w_2)^{1/2} h^{-1}$$

$$z_3 q = y_2 (w_1)^{1/2} h^{-2}$$

Appendix B: Equation 5

Following the approach established in the previous Technical Report, we let $s = z_1/z_3$. Then we divide the first equation by the third in the set of *Appendix B: Equation 2*:

$$\frac{z_1 q}{z_3 q} = \frac{y_1}{y_2 h^{-2}}$$

which gives

$$s = z_1/z_3 = y_1 h^2/y_2$$

Appendix B: Equation 6

We also multiply the third equation in the set of *Appendix B: Equation 2* by the term $z_1 q$, to yield

$$z_1 z_3 q^2 = y_1 y_2 w_1 h^{-2}$$

Appendix B: Equation 7

Refer now to the second equation of set *Appendix B: Equation 2*:

$$z_2 q = (y_1 y_2 w_2)^{1/2} h^{-1}$$

Appendix B: Previous Equation 2; 2nd equation of set

We square both sides to obtain

$$z_2^2 q^2 = y_1 y_2 w_2 h^{-2}$$

Appendix B: Equation 8

We can rewrite this as

$$\frac{z_2^2 q^2}{w_2} = y_1 y_2 h^{-2}$$

Appendix B: Equation 9

We can substitute this into *Appendix B: Equation 7* and divide through both sides by q^2 to obtain

$$z_1 z_3 = z_2^2 \frac{w_1}{w_2}$$

Appendix B: Equation 10

We recall from *Equation 1-6* that:

$$x_1 = y_1 + y_2 = z_1 + z_2 + z_3 + z_5$$

Also, since at $x_1 = \frac{1}{2}$, we have $z_2 = z_5$, we rewrite the previous equation as

$$x_1 = \frac{1}{2} = y_1 + y_2 = z_1 + 2z_2 + z_3$$

Appendix B: Equation 11

Then we can write

$$2z_2 = \frac{1}{2} - z_1 - z_3$$

Appendix B: Equation 12

Divide through by 2, and square both sides to obtain

$${z_2}^2 = \frac{1}{16}[1 - 2z_1 - 2z_3]^2$$

Appendix B: Equation 13

Substitute this into *Appendix B: Equation 10* to obtain

$$z_1 z_3 = z_2^2 \frac{w_1}{w_2} = \frac{1}{16}[1 - 2z_1 - 2z_3]^2 \frac{w_1}{w_2}$$

Appendix B: Equation 14

Now, divide through by z_3^2 and multiply both sides by w_2/w_1 to obtain

$$\frac{z_1}{z_3}\frac{w_2}{w_1} = \frac{1}{16}\left[\frac{1}{z_3} - \frac{2z_1}{z_3} - 2\right]^2$$

Appendix B: Equation 15

We had previously defined: $s = z_1/z_3$. We now substitute this into *Appendix B: Equation 15* to obtain

$$s\frac{w_2}{w_1} = \frac{1}{16}\left[\frac{1}{z_3} - 2s - 2\right]^2$$

Appendix B: Equation 16

We now need to express the fraction variables w_2 and w_1 in terms of z_3. To do this, we recall from *Equation 1-6* that

$$w_1 = z_1 + z_3$$

$$w_2 = z_2 + z_5$$

Further, at equilibrium, we have $z_2 = z_5$ so that $w_2 = 2z_2$.

We have previously established that, at equilibrium,

$$2z_2 = \frac{1}{2} - z_1 - z_3$$

Thus, we can write

$$w_2 = \frac{1}{2} - z_1 - z_3$$

Thus we have

$$\frac{w_2}{w_1} = \frac{2z_2}{z_1 + z_3} = \frac{\frac{1}{2} - z_1 - z_3}{z_1 + z_3} = \frac{(1 - 2z_1 - 2z_3)}{2(z_1 + z_3)}$$

We divide through, top and bottom, by z_3, and recall that we defined $s = z_1/z_3$, to obtain

$$\frac{w_2}{w_1} = \frac{\left(\frac{1}{z_3} - \frac{2z_1}{z_3} - 2\right)}{2\left(\frac{z_1}{z_3} + 1\right)} = \frac{\left(\frac{1}{z_3} - 2s - 2\right)}{2(s+1)}$$

Appendix B: Equation 17

Substituting this into *Appendix B: Equation 16*, we obtain

$$s\frac{\left(\frac{1}{z_3} - 2s - 2\right)}{2(s+1)} = \frac{1}{16}\left[\frac{1}{z_3} - 2s - 2\right]^2$$

Appendix B: Equation 18

Which we can immediately rewrite as

$$s\frac{1}{(s+1)} = \frac{1}{8}\left[\frac{1}{z_3} - 2s - 2\right]$$

Appendix B: Equation 19

We now solve for s in terms of z_3. Cross-multiplication gives

$$8s = (s+1)\left[\frac{1}{z_3} - 2s - 2\right]$$

We can rewrite this to express $1/z_3$ in terms of s.

$$\frac{8s}{(s+1)} = \frac{1}{z_3} - 2s - 2$$

or

$$\frac{1}{z_3} = \frac{8s}{(s+1)} + 2s + 2 = \frac{2}{(s+1)}[4s + (s+1)^2]$$

or

$$\frac{1}{z_3} = \frac{2}{(s+1)}[4s + s^2 + 2s + 1] = \frac{2}{(s+1)}[s^2 + 6s + 1]$$

Appendix B: Equation 20

We recall *Appendix B: Equation 6*

$$s = z_1/z_3 = y_1 h^2/y_2$$

Previous Appendix B: Equation 6

We rewrite this to obtain an expression for h^2

$$h^2 = s\, y_2/y_1$$

Appendix B: Equation 21

We now wish to express y_2/y_1 in terms of *s* and z_3.

We r recall *Equation 1-6*, giving expressions for the y_i:

$$y_1 = z_1 + z_2$$

$$y_2 = z_2 + z_4 = z_3 + z_5$$

We also recall that at equilibrium, from *Appendix B: Equation 3*, we have

$$z_3 = z_4$$

and from previous work that

$$2z_2 = \tfrac{1}{2} - z_1 - z_3$$

This allows us to write

$$y_1 = z_1 + z_2 = z_1 + \frac{1}{2}\left[\tfrac{1}{2} - z_1 - z_3\right]$$

$$y_2 = z_2 + z_3 = \frac{1}{2}\left[\tfrac{1}{2} - z_1 - z_3\right] + z_3$$

Appendix B: Equation 22

We combine this in an expression for y_2/y_1

$$\frac{y_2}{y_1} = \frac{\frac{1}{2}\left[\frac{1}{2} - z_1 - z_3\right] + z_3}{z_1 + \frac{1}{2}\left[\frac{1}{2} - z_1 - z_3\right]} = \frac{\left[\frac{1}{2} - z_1 - z_3\right] + 2z_3}{2z_1 + \left[\frac{1}{2} - z_1 - z_3\right]}$$

or, combining terms,

$$\frac{y_2}{y_1} = \frac{\frac{1}{2} - z_1 + z_3}{\frac{1}{2} + z_1 - z_3}$$

or, multiplying top and bottom by 2, we obtain

$$\frac{y_2}{y_1} = \frac{1 - 2z_1 + 2z_3}{1 + 2z_1 - 2z_3}$$

and dividing through by z_3, we obtain

$$\frac{y_2}{y_1} = \frac{\frac{1}{z_3} - \frac{2z_1}{z_3} + 2}{\frac{1}{z_3} + \frac{2z_1}{z_3} - 2} = \frac{\frac{1}{z_3} - 2s + 2}{\frac{1}{z_3} + 2s - 2}$$

Referring now to *Appendix B: Equation 21*, we have

$$h^2 = s\, y_2/y_1 = s\frac{\frac{1}{z_3} - 2s + 2}{\frac{1}{z_3} + 2s - 2}$$

Appendix B: Equation 23

We recall *Appendix B: Equation 20*

$$\frac{1}{z_3} = \frac{2}{(s+1)}\left[s^2 + 6s + 1\right]$$

We make the appropriate substitutions from *Appendix B: Equation 20* into *Appendix B: Equation 23* to obtain

$$h^2 = s\frac{\frac{1}{z_3} - 2s + 2}{\frac{1}{z_3} + 2s - 2} = s\frac{\frac{2}{(s+1)}\left[s^2 + 6s + 1\right] - 2s + 2}{\frac{2}{(s+1)}\left[s^2 + 6s + 1\right] + 2s - 2}$$

Appendix B: Equation 24

Our first step is to multiply through in *Appendix B: Equation 24*, top and bottom, by *(s+1)*, and doing some simplification, to obtain

$$h^2 = s\frac{[s^2 + 6s + 1] - (s - 1)(s + 1)}{[s^2 + 6s + 1] + (s - 1)(s + 1)}$$

or

$$h^2 = s\frac{s^2 + 6s + 1 - s^2 + 1}{s^2 + 6s + 1 + s^2 - 1}$$

or

$$h^2 = s\frac{6s + 2}{2s^2 + 6s} = \frac{3s + 1}{s + 3}$$

Appendix B: Equation 25

We can work with this equation to obtain an expression for *s* in terms of *h*.

$$h^2(s + 3) = 3s + 1$$

or

$$h^2 s + 3h^2 - 3s - 1 = 0$$

or

$$(h^2 - 3)s = 1 - 3h^2$$

or

$$s = \frac{1 - 3h^2}{h^2 - 3}$$

Appendix B: Equation 26

Once again, we recall *Appendix B: Equation 20*

$$\frac{1}{z_3} = \frac{2}{(s + 1)}[s^2 + 6s + 1]$$

We substitute from *Appendix B: Equation 26* into this equation to obtain

$$\frac{1}{z_3} = \frac{2}{\left(\frac{1 - 3h^2}{h^2 - 3} + 1\right)}\left[\left(\frac{1 - 3h^2}{h^2 - 3}\right)^2 + 6\frac{1 - 3h^2}{h^2 - 3} + 1\right]$$

Appendix B: Equation 27

We multiply through, top and bottom, by $(h^2 - 3)^2$

$$\frac{1}{z_3} = \frac{2(h^2-3)^2}{(h^2-3)(1-3h^2+h^2-3)}\left[\left(\frac{1-3h^2}{h^2-3}\right)^2 + 6\frac{1-3h^2}{h^2-3} + 1\right]$$

or

$$\frac{1}{z_3} = \frac{2(h^2-3)^2}{(h^2-3)(-2h^2-2)}\left[\left(\frac{1-3h^2}{h^2-3}\right)^2 + 6\frac{1-3h^2}{h^2-3} + 1\right]$$

or

$$\frac{1}{z_3} = \frac{(-1)}{(h^2-3)(h^2+1)}[(1-3h^2)^2 + 6(1-3h^2)(h^2-3) + (h^2-3)^2]$$

Appendix B: Equation 28

We simplify the terms in the RHS

$$(1-3h^2)^2 = 1 - 6h^2 + 9h^4$$

$$6(1-3h^2)(h^2-3) = 6(h^2 - 3 - 3h^4 + 9h^2) = 6(-3h^4+10h^2-3) = -18h^4 + 60h^2 - 18$$

$$(h^2-3)^2 = h^4 - 6h^2 + 9$$

Combining, we obtain

$$\begin{aligned}(1-3h^2)^2 + 6(1-3h^2) + (h^2-3)^2 &= 1 - 6h^2 + 9h^4 - 18h^4 + 60h^2 - 18 + h^4 - 6h^2 + 9 \\ &= (9-18+1)h^4 + (-6+60-6)h^2 + (1-18+9) = -8h^4 + 48h^2 - 8 \\ &= 8(-h^4 + 6h^2 - 1)\end{aligned}$$

Substitute this into *Appendix B: Equation 28* to obtain

$$\frac{1}{z_3} = \frac{(-1)}{(h^2-3)(h^2+1)}[8(-h^4+6h^2-1)]$$

or

$$\frac{1}{z_3} = \frac{8[h^4-6h^2+1]}{(h^2-3)(h^2+1)}$$

or

$$z_3 = \frac{(h^2-3)(h^2+1)}{8[h^4-6h^2+1]}$$

Appendix B: Equation 29

We note that this equation will give discontinuities when the denominator is zero.

However, in the region where *h=1* (the interaction energy is zero), this gives the expected behavior:

$$(z_3)_{h=1} = \frac{(1^2-3)(1^2+1)}{8[1^4-6\times 1^2+1]} = \frac{(-2)(2)}{8[1-6+1]} = \frac{(-4)}{8[-4]} = \frac{1}{8} = 0.125$$

The value of 0.125 is the expected result when *h=1*.

Further, from *Appendix B: Equation 26* and *Appendix B: Equation 29*

$$z_1 = sz_3 = \frac{1-3h^2}{h^2-3}\frac{(h^2-3)(h^2+1)}{8[h^4-6h^2+1]}$$

Appendix B: Replicate Eqn. 3

Or

$$z_1 = \frac{(1-3h^2)(h^2+1)}{8[h^4-6h^2+1]}$$

Appendix B: Equation 30

We further have from *Equation 1-6*

$$y_1 = z_1 + z_2$$

$$y_2 = z_2 + z_4 = z_3 + z_5$$

$$y_3 = z_5 + z_6$$

Appendix B: Replicate Eqn. 2-6 (partial set)

Since at $x_1 = x_2$, we also have (see *Appendix B: Equation 3*) $z_3 = z_4$, we can rewrite the equation for y_2 as

$$y_2 = z_2 + z_4 = z_2 + z_3$$

or

$$y_2 = \tfrac{1}{4}(1-2z_1-2z_3) + z_3$$

or

$$y_2 = \tfrac{1}{4}(1-2z_1+2z_3)$$

Appendix B: Equation 31

Further, at $x_1 = 0.5 = y_1 + y_2$, we can write

$$y_1 = 0.5 - y_2 = \frac{1}{2} - \tfrac{1}{4}(1 - 2z_1 + 2z_3)$$

or

$$y_1 = \tfrac{1}{4}(1 + 2z_1 - 2z_3)$$

Appendix B: Equation 32

Further

$$z_2 = [1 - 2z_1 - 2z_3]/4$$

Appendix B: *Equation 2-19* (from main body of text)

We have an analytic solution for the full set of fraction variables only at $x_1 = x_2 = 0.5$, which is

$$z_1 = z_6$$

$$z_2 = z_6$$

$$z_3 = z_4$$

$$w_1 = w_3$$

$$y_1 = y_3$$

$$y_3 = 0.5 - y_2$$

$$w_3 = 0.5 - w_2$$

Appendix B: Replicate Equation 2-21 (from main body of text)

and the remaining fraction variables are readily obtained.[4]

[4] Details of the analytic solution were originally published in: Maren, A.J. (1981). *Theoretical Models for Solid State Phase Transitions*, Ph.D. Dissertation, Arizona State University. These results are revised and updated.