The Cluster Variation Method I: 1-D Single Zigzag Chain

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

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Abstract

This *Technical Report* presents the equations for a 1-D zigzag chain of bistate units using the Cluster Variation Method, a hierarchy of approximate variational methods for representing the equilibrium state of discrete systems, and offering improvement over the classic Bethe-Peierls approximation and the mean-field approximation by using configurational variables as well as state values for determining system entropy. 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:

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

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

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

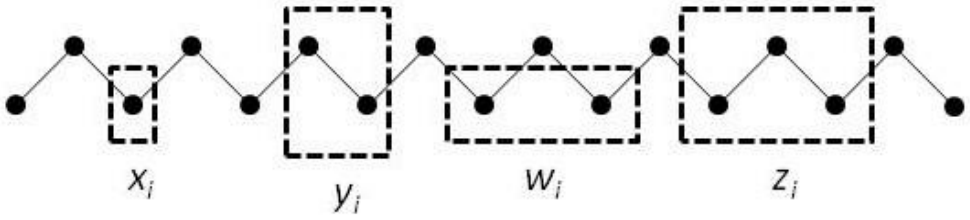

Figure 2: Single zigzag chain; the fraction variables y_i are nearest-neighbors, and the w_i are next-nearest-neighbors, which are "proximal" to their neighbors across the upper and lower portions of the chain respectively. The fraction variables z_i are comprised of any consecutive triplet.

[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.

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

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

We consider first the entropy of a single zigzag chain, as shown previously.

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

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

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:

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

Equation 2-2

We substitute from *Equation 2-2* to *Equation 1-8* 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.

2.2 Free Energy Minimization in the Single ZigZag Chain

For a one-dimensional system (single zigzag chain), the free energy is

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

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

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

Equation 2-4

where μ and λ are Lagrange multipliers.

Taking the derivative of G_{1-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:

$$z_1 q = y_1$$

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

$$z_3 q = y_2 e^{-\beta\epsilon/2} e^{-2\lambda}$$

$$z_4 q = y_2 e^{-\beta\epsilon/2} e^{2\lambda}$$

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

$$z_6 q = y_3$$

Equation 2-5

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

For the system where $x_1 = x_1 = 0.5$ and $\lambda = 0$, *Equation 2-5* and *Equation 1-6* 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

$$h^2 = s\frac{1 + (s)^{1/2}}{s + (s)^{1/2}}$$

or

$$s = h^4$$

Equation 2-6

and

$$z_1 = sz_3$$

Equation 2-7

and

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

Equation 2-8

and

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

Equation 2-9

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 2-10

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 single zigzag chain.[4]

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

[4] The discussion of the analytic solution in Section 4 is taken from a blogpost written by A.J. Maren on Dec. 8, 2008, Analytic Single-Point Solution for the Cluster Variation Method Variables at x_1=x_2=0.5, http://www.aliannajmaren.com/2011/12/08/analytic-single-point-solution-for-cluster-variation-method-variables-at-x1x20-5/ , accessed March 12, 2014.

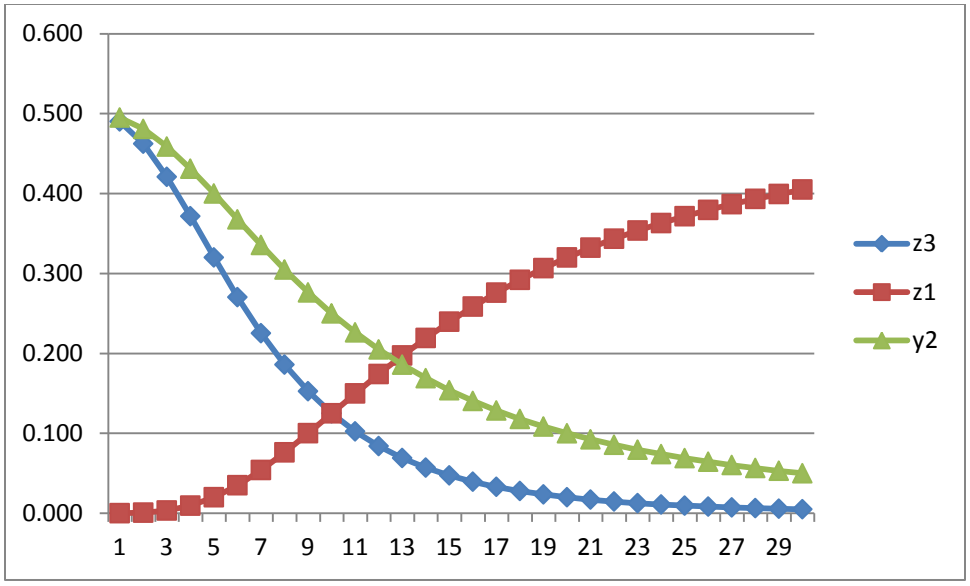

Figure 3: Results for three configuration variables, z3, z1, & y2. Values for h*10 are plotted along the x-axis.

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.

Consider the case of a 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. We observe this on the RHS of the above graph. This is the case where as $h = e^{\beta\epsilon/4}$ moves into the positive range (0-3), we see that y_2 and z_3 fall towards zero. In particular, z_3 becomes very small. Correspondingly, this is also the situation in which $z_1 = z_6$ becomes large; we see z_1 taking on values > 0.4 when $h > 2.9$.

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 β = *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 (0.1 – 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 pairwise combination y_2 (A-B) actually increases slightly beyond its nominal expectation (when there is no interaction energy), and goes above 0.25, notably when *h* is in the range of 0.1 and smaller. Also, as expected, the value for z_1 (A-A-A triplets) also drops towards zero – triplets of like units are suppressed when the interaction energy between units is positive.

Somewhat surprisingly, z_3 (A-B-A triplets) also decreases as *h* approaches 0.1. This means that the increase to above-nominal distributions for the CVM variable goes to z_2 (A-A-B). Given that this is an even distribution of A and B units ($x_1 = x_2 = 0.5$), another way to think of the far LHS is when the temperature is very large. (We then have the exponent of a negative interaction energy over a large temperature, and can think of the increased temperature as producing greater "disorder" in the system – moving us away from the highly structured A-B-A-B-A order that would otherwise exist if y_2 (A-B) predominated with no other influence.

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). *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:

$$z_1 q = y_1$$

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

$$z_3 q = y_2 e^{-\beta\epsilon/2} e^{-2\lambda}$$

$$z_4 q = y_2 e^{-\beta\epsilon/2} e^{2\lambda}$$

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

$$z_6 q = y_3$$

Replicate Equation 2-5 (from main body of text)

We find these relationships by differentiating the free energy expression $G_{1\text{-}D}$ with respect to each of the cluster variables and setting the result to zero.

We begin with the free energy expression for the 1-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 one-dimensional system (single zigzag chain), the free energy is

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

Replicate Equation 2-4 (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 $G_{1\text{-}D}$ on z_1.

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

Appendix A: Equation 1

We find the following:

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

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:

$$y_1 = z_1 + z_2$$

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

$$y_3 = z_5 + z_6$$

Replicate portion of Equation 2.6

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

$$0 \equiv \frac{\partial G_{1-D}}{\partial z_1} = 2\left[-\frac{\partial}{\partial z_1}Lf(y_1) + \frac{\partial}{\partial z_1}Lf(z_1)\right] - \mu\beta$$

or

$$0 \equiv \frac{\partial G_{1-D}}{\partial z_1} = 2\left[-ln(y_1)\frac{\partial y_1}{\partial z_1} + ln(z_1)\frac{\partial z_1}{\partial z_1}\right] - \mu\beta$$

or

$$0 \equiv \frac{\partial G_{1-D}}{\partial z_1} = 2\left[-ln(y_1)\frac{\partial y_1}{\partial z_1} + ln(z_1)\right] - \mu\beta$$

or

$$0 \equiv \frac{\partial G_{1-D}}{\partial z_1} = 2[-ln(y_1) + ln(z_1)] - \mu\beta$$

Appendix A: Equation 3

Thus we have

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

or

$$ln(z_1) - \frac{\mu\beta}{2} = ln(y_1)$$

Appendix A: Equation 4

Taking the exponent of both sides, we have

$$z_1 \exp\left(\frac{-\mu\beta}{2}\right) = y_1$$

Appendix A: Equation 5

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

$$z_1 \mathrm{q} = y_1$$

Appendix A: Equation 6

Now, we compute the dependence of $G_{1\text{-}D}$ 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

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

Appendix A: Equation 7

Simplifying, we have

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

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

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

or

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

Appendix A: Equation 11

Rearranging terms, we have

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

Appendix A: Equation 12

We take the exponent of both sides to obtain

$${z_2}^2 \exp(-\mu\beta) = y_1 y_2 exp\left(-\frac{\beta\epsilon}{2}\right) exp(2\lambda)$$

Appendix A: Equation 13

We take the square root of both sides to obtain

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

Appendix A: Equation 14

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

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

Our third step in this Appendix is to compute the dependence of $G_{1\text{-}D}$ 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

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

Appendix A: Equation 15

Doing the most obvious simplifications, we have

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

Appendix A: Equation 16

From *Equation 1-6*, we recognize that the only dependence of the y_i on z_3 is with y_2. Specifically, we had previously identified that $2y_2 = z_2 + z_4 + z_3 + z_5$ (*Appendix A: Equation 9*).

This gives us

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

or

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

or

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

or

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

Appendix A: Equation 17

We can reorganize this as

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

Appendix A: Equation 18

We take the exponent of both sides to obtain

$$z_3 \exp\left(-\frac{\mu\beta}{2}\right) = y_2 exp\left(-\frac{\beta\epsilon}{2}\right) exp(-2\lambda)$$

or

$$z_3 \mathrm{q} = y_2 exp\left(-\frac{\beta\epsilon}{2}\right) exp(-2\lambda)$$

Appendix A: Equation 19

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 2-5*.

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

This Appendix takes the results given in Section 3, 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:

$$z_1 q = y_1$$

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

$$z_3 q = y_2 e^{-\beta\epsilon/2} e^{-2\lambda}$$

$$z_4 q = y_2 e^{-\beta\epsilon/2} e^{2\lambda}$$

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

$$z_6 q = y_3$$

Appendix B: Replicate Equation 2-5 (from main body of text)

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

$$z_1 q = y_1$$

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

$$z_3 q = y_2/h^2$$

$$z_4 q = y_2/h^2$$

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

$$z_6 q = y_3$$

Appendix B: Equation 1

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 2

Let $s = z_1/z_3$. Then we divide the first equation by the third in the set of Eqns. B-1:

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

which gives

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

Appendix B: Equation 3

We also multiply the third equation in the set of Eqns. A-1 by the term $z_1 q$, which is identical with y_1, to yield

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

Appendix B: Equation 4

Refer now to the second equation of set B-1:

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

Appendix B: Previous Equation 1; 2nd equation of set

We square both sides to obtain

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

Appendix B: Equation 5

We can substitute this into Eqn. B-4 and divide through both sides by $q^2$to obtain

$$z_1 z_3 = z_2^2$$

Appendix B: Equation 6

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 7

Then we can write

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

Appendix B: Equation 8

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 9

Substitute this into B-6 to obtain

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

Appendix B: Equation 10

Now, divide through by z_3^2 to obtain

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

Appendix B: Equation 11

We had previously defined: $s = z_1/z_3$. We now substitute this into Eqn. B-11 to obtain

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

Appendix B: Equation 12

We now solve for s in terms of z_3. The first step is to multiple through by 16 and to expand the terms on the RHS.

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

or

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

or

$$16s = \left(\frac{1}{z_3}\right)^2 - \frac{4}{z_3}[s + 1] + 4[s + 1]^2$$

or

$$16s = \frac{1}{z_3^2} - \frac{4(s+1)}{z_3} + 4(s+1)^2$$

Appendix B: Equation 13

Collect terms to obtain a quadratic in $(1/z_3)$

$$\left(\frac{1}{z_3}\right)^2 - 4(s+1)\frac{1}{z_3} + 4(s+1)^2 - 16s = 0$$

Appendix B: Equation 14

We now solve this quadratic to obtain an expression for $(1/z_3)$, using the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Apply this to:

$$\left(\frac{1}{z_3}\right)^2 - 4(s+1)\frac{1}{z_3} + 4(s+1)^2 - 16s = 0$$

to obtain

$$\frac{1}{z_3} = \left(\frac{1}{2}\right)\left[4(s+1) \pm (16(s+1)^2 - 4[4(s+1)^2 - 16s])^{1/2}\right]$$

or

$$\frac{1}{z_3} = 2(s+1) \pm \left(\frac{1}{2}\right)(16(s+1)^2 - 4[4(s+1)^2 - 16s])^{1/2}$$

or

$$\frac{1}{z_3} = 2(s+1) \pm \left(\frac{1}{2}\right)(16(s+1)^2 - 16(s+1)^2 - 4[-16s])^{1/2}$$

or

$$\frac{1}{z_3} = 2(s+1) \pm \left(\frac{1}{2}\right)(4[16s])^{1/2}$$

or

$$\frac{1}{z_3} = 2(s+1) \pm 4(s)^{1/2}$$

Appendix B: Equation 15

We recall that $1/z_3$ is close to 8. (z_3 itself, being a triplet distribution variable, occurs about 1/8 of the time.) Also, we defined: $s = z_1/z_3$, and z_1 occurs with about the same frequency as z_3 (especially when at $x_1 = x_2$), so that *s* is approximately 1.

Thus, inserting approximate values into Eqn. B-15, we obtain

$$8 \cong 2(2) \pm 4(1)^{1/2}$$

Appendix B: Equation 16

which we can rewrite as

$$2 \cong 1 \pm (1)^{1/2}$$

Appendix B: Equation 17

which means that we must take the positive term on the RHS. This gives us

$$\frac{1}{z_3} = 2(s+1) + 4(s)^{1/2}$$

Appendix B: Equation 18

This gives an expression for $1/z_3$ in terms of: $s = z_1/z_3$. We will use this as a substitution term to determine *h*. To do this, we begin by getting expressions for z_2, y_2, and y_1.

We recall Eqn. B-8:

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

or

$$z_2 = \tfrac{1}{4}(1 - 2z_1 - 2z_3)$$

Appendix B: Equation 19

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 Eqn. B-2) $z_3 = z_4$, 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 20

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 21

Refer now to *Appendix B: Equation 3* which gave:

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

Appendix B: Equation 3 (replicate)

which we can rewrite to give us h^2:

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

Appendix B: Equation 22

We make substitutions using Eqns. B-20 and B-21 to yield

$$h^2 = s\frac{\frac{1}{4}(1 - 2z_1 + 2z_3)}{\frac{1}{4}(1 + 2z_1 - 2z_3)} = s\frac{1 - 2z_1 + 2z_3}{1 + 2z_1 - 2z_3}$$

Appendix B: Equation 23

Divide through the top and bottom of the RHS now by z_3 and recall that $s = z_1/z_3$ to yield

$$h^2 = s\frac{\frac{1}{z_3} - 2s + 2}{\frac{1}{z_3} + 2s - 2}$$

Appendix B: Equation 24

Now, recall that we have obtained an expression for $1/z_3$ in terms of: $s = z_1/z_3$.

$$\frac{1}{z_3} = 2(s + 1) + 4(s)^{1/2}$$

Appendix B: Equation 18 (replicate)

Substitute from Eqn. B-18 into B-24 to obtain:

$$h^2 = s\frac{2(s + 1) + 4(s)^{1/2} - 2s + 2}{2(s + 1) + 4(s)^{1/2} + 2s - 2}$$

Appendix B: Equation 25

We combine terms and divide through by constants to give

$$h^2 = s\frac{1 + (s)^{1/2}}{s + (s)^{1/2}}$$

or

$$h^2 = s\frac{1 + s^{1/2}}{s^{1/2}(1 + s^{1/2})}$$

or

$$h^2 = s^{1/2} = \left(\frac{z_1}{z_3}\right)^{1/2}$$

or

$$s = h^4$$

Appendix B: Equation 26

This gave us an expression for s in terms of h. We can substitute this into Eqn. B-18.

$$\frac{1}{z_3} = 2(s+1) + 4(s)^{1/2}$$

Appendix B: Equation B-18 (replicate)

Substituting from Eqn. B-26 into B-18, we get

$$\frac{1}{z_3} = 2(h^4+1) + 4(h^4)^{1/2}$$

or

$$\frac{1}{z_3} = 2(h^4+1) + 4h^2$$

or

$$\frac{1}{z_3} = 2(h^2+1)^2$$

or

$$z_3 = \frac{1}{2(h^2+1)^2}$$

Appendix B: Equation 27

Further,

$$z_1 = sz_3 = h^4 z_3$$

Appendix B: Replicate Eqn. B-3

and

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

Appendix B: Replicate *Equation 2-8*

And

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

Appendix B: Replicate Equation 2-9 (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 2-10 (from main body of text)

and the remaining fraction variables are readily obtained.[5]

[5] 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.